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THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: BASIC THEORY

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1. *Introduction*

The first great step towards the development of a satisfactory theory of the specific heats of solids was taken by Einstein in 1907 when he showed that the acceptance of the hypothesis of radiation quanta involves as a necessary consequence that the mechanical energy of the vibrations of the atoms in a solid must also be regarded as consisting of discrete units or quanta proportional to the frequency of vibration. A quantitative relationship between the heat content of a solid and the "frequency spectrum" of its internal vibrations was thus indicated. The evaluation of the thermal energy of a solid accordingly depends on a determination of its vibration spectrum, in other words, a knowledge of the frequencies of atomic vibration and of the manner in which the available degrees of freedom are distributed amongst them. This is a problem of some difficulty to the solution of which there are two distinct methods of approach. The first is the phenomenological one, namely that of obtaining the desired information in some independent fashion, *e.g.*, by spectroscopic research. The other is the *a priori* method of finding the possible modes of vibration from a knowledge of the crystal structure and the forces acting between the atoms by a dynamical investigation. To the genius of Einstein we owe the first indication of both of these methods of approach to the specific heat problem. The reconciliation of the results obtained by the two methods with each other and with the specific heat determinations over a wide range of temperatures is obviously of the highest importance for a proper understanding of the physics of the solid state.

2. *Nature of the Thermal Agitation in Crystals*

A crystal is a periodic three-dimensional grouping in space of an immense number of atoms, ions or molecules held to each other by the interatomic or intermolecular forces. The structure being on an exceedingly small scale, the number of cells of the crystal lattice included in any volume of macroscopic dimensions is enormously large. This fact makes it possible to divide the possible modes of thermal agitation in a crystal sharply into two classes. *The vibrations of the first class* are on a relatively large scale and may be described without any reference to the fine structure of the solid. These are

the elastic vibrations of the crystal; their modes and frequencies are determined by the velocity of propagation of the elastic waves in it and the shape and dimensions of the external boundary of the solid. *The vibrations of the second class* are essentially dependent on the fine structure of the crystal. In view of the tremendous disparity in size between the lattice cells and the macroscopic dimensions of the solid, the shape and dimensions of the crystal are without influence on vibrations of this kind. They may be visualized and described as time-periodic variations from the static crystal structure. The vibrations of the first class involve oscillatory movements of large groups of atoms, while those of the second involve displacements in the relative positions of neighbouring atoms. The frequencies of vibration of the second class would therefore be much greater than those of the first. The dividing line between the two classes of vibration is most appropriately drawn at a frequency for which the wave-lengths of the elastic vibration are just large enough to justify the fine structure of the crystal being ignored.

The division here made of the possible modes of vibration of the crystal into two classes corresponds also to a fundamental difference in the character of the vibration spectrum in the two regions of frequency. Considering the elastic vibrations, it is evident that the larger the crystal, the smaller would be the frequency differences between the successive possible modes of vibration. Hence, *the elastic vibrations of a crystal of macroscopic dimensions give a continuous spectrum of frequencies.* The position is completely different in respect of the second class of vibrations. Here, as already remarked, the size of the crystal is not a relevant factor. As the vibrations involve periodic variations in the crystal structure, they may be pictured as forming dynamic repetition patterns in space related to the crystal structure in some simple way. The principal modes of vibration would be those in which the atomic movements occur in identically the same fashion in every lattice cell of the crystal. Less important, but nevertheless requiring consideration are periodic movements of a more general kind, *viz.*, oscillations which have identically the same form in the cells of a superlattice which is a repetition on a larger scale of the static crystal structure, the spacings being an integral multiple thereof. All such vibrations would have uniquely defined frequencies, in other words, they would be monochromatic, and if the cells of the superlattice are not too large, they would also be finite in number. *The vibrations of the second class would thus appear as a set of discrete and enumerable monochromatic frequencies in the infra-red region of the spectrum.*

The manner in which the thermal energy of the crystal would be distributed amongst the various possible modes of vibration can now be readily visualized. The largest part of the thermal energy would be carried by the

modes of vibration which have been referred to as the principal lattice frequencies. These are obtained by considering a lattice cell having all the symmetry elements present in the crystal and thus fully representative of it. By applying the appropriate geometric and analytical methods, we find the number, character and frequencies of the various modes of vibration of the p atoms located in the cell. Such an analysis would yield $(3p - 3)$ modes of internal vibration and 3 translations for the cell as a whole. If p be fairly large, as is the case with the vast majority of crystals, the $(3p - 3)$ degrees of freedom appearing as vibrations would greatly exceed in number the 3 degrees of translation. The next stage in the analysis would be to consider a superlattice of which the cells have twice the edge length of the lattice cells first chosen. Applying similar methods to it, we would have $(24p - 3)$ modes of internal vibration of the atoms included in the cell and 3 translations. The former would naturally include the $(3p - 3)$ modes of vibrations already considered, besides others approaching them in character, and we would obtain also new modes of vibration previously reckoned as simple translations of the unit cell. We may, if necessary, similarly proceed to consider a cell thrice as large which would give us $(81p - 3)$ modes of internal vibration and 3 translations, or even a cell four times as large which would give us $(192p - 3)$ internal vibrations and 3 translations. These refinements should, however, be unnecessary except for crystals in which p is a small number and usually not even in their case. Thus, when the analysis is carried sufficiently far, all the modes of vibration which make any sensible contribution to the thermal energy of the crystal may be identified, and the residue associated with the energy of the elastic vibrations of undefined frequency may be ignored. The number of the vibrations of the latter kind bears to the total number of degrees of atomic freedom a ratio of the same order of magnitude as the ratio of the volume of an individual atom to the cube of the limiting wave-length. When, therefore, the wave-length limit is even moderately large in relation to the lattice spacings of the crystal, the energy of such vibrations is a negligible fraction of the whole.

The results of our discussion may be summed up as follows: *In evaluating the thermal energy of a crystalline solid, we are only concerned with the discrete or monochromatic frequencies appearing in its infra-red spectrum which owe their origin to the displacements of the atoms from their positions of equilibrium in the characteristic structure of the crystal: the elastic vibrations which involve only a general distortion of the lattice may be left out of account altogether.*

3. The Specific Heat Theory of Debye

The result stated above is in direct contradiction with the assumptions made in the theory of specific heats of solids due to Debye. The latter

identifies the thermal energy of the crystal *ab initio* with that of the elastic vibrations. A property connected in the closest manner with the atomic or molecular structure of the solid is thereby sought to be interpreted in terms of purely molar concepts, namely density, elasticity and sound velocities, thus reversing the usual idea of a physical explanation. No theoretical or experimental justification can, however, be found for the basic assumption made in the Debye theory that the vibrations carrying the thermal energy are of the elastic solid type. The fact that elastic vibrations travel with a high velocity, while heat energy does not travel at all but only diffuses with extreme slowness, is sufficient in itself to make such an identification questionable. That the extrapolation, made in the Debye theory, of ideas derived from the physics of continuous media to the physics of atomic structures is not justifiable is indicated by the simple mechanical analogy of a periodically loaded string. Consider a string of finite length under tension T to which m loads, each of mass μ are attached at regular intervals a apart. The displacement of the rth load in the sth mode of vibration is given by the formula:—

$$\psi_r = P_s \cdot \sin \frac{(r-1)\, s\pi}{m+1} \cdot \cos (n_s t - \epsilon_s) \tag{1}$$

where

$$n_s = 2\sqrt{\frac{T}{\mu a}} \cdot \sin \frac{s\pi}{2(m+1)} \tag{2}$$

Provided the integer s appearing in these formulæ is small compared with m, the vibrations approximate in form to those of a uniform string. As s increases, however, the vibrations resemble less and less those of a uniform string, until when $s = \frac{1}{2}(m+1)$ all resemblance disappears, the mode of vibration then being determined entirely by the periodicity of the loading. In other words, as the wave-length of the transverse oscillations is diminished to the point at which it becomes four times the interval between the loads, we are no longer concerned with the behaviour of a uniform string but have to consider, instead, the characteristic vibrations of a periodically loaded string. It may be reasonably inferred from this analogy that in the case of a three-dimensional periodic structure, the ideas based on the physics of continuous media cease to be appropriate in considering vibrations of high frequency in which the atomic architecture of the crystal is specifically involved.

While the specific heat curve can be uniquely derived from the vibration spectrum, a knowledge of the specific heat data is obviously insufficient for a determination of the vibration spectrum. That the Debye formula with an appropriately chosen limiting frequency fits the specific heat data in certain cases is not therefore a proof of the correctness of the basic assumptions of

the theory, and cannot be regarded as an indication that the vibration spectrum in these cases bears any resemblance to that postulated in the theory. It may be recalled that the Debye function is the integrated sum of a continuous sequence of Einstein functions over a range of frequencies with weights proportional to their squares and a sharp cut-off at an upper limit. Experimental data which fit a Debye function should therefore equally be capable of being represented as the sum of a finite number of Einstein functions with appropriate frequencies and weight factors. It is very significant also from our present point of view, that the Debye formula fails to represent correctly the specific heat of several elements crystallising in the cubic system. For, this indicates that the success of the formula in other cases is largely accidental. A feature of the Debye theory which is often emphasised is that the elastic constants calculated from the specific heats come out of the right order of magnitude. As was pointed out in Einstein's earliest papers, however, the existence of approximate relations between the atomic frequencies and the elastic constants is indicated by elementary considerations. No special significance can therefore attach to this feature of the Debye theory.

4. Born's Theory of the Cyclic Lattice

While the Debye theory ignores the discrete structure of the crystal, the crystal dynamics of Max Born and his school formally takes account of it. Born's theory, however, rests on his postulate of the " cyclic lattice ", in other words on his assumption that all the atomic displacements are periodic in a volume having the same shape as the elementary cell of the lattice but of very great size in comparison with it. The postulate makes no distinction between the atomic vibrations of high frequency and the elastic vibrations of low frequency, and assumes that all the possible vibrations have wave-lengths which are sub-multiples of the external dimensions of the crystal. It is readily seen that this postulate is unjustifiable. While the external boundary of the solid acts as a reflecting barrier for the elastic waves and thereby determines the frequencies of elastic vibrations, it can have no such influence on the internal vibrations of the crystal lattice. These latter have frequencies which are determined by the crystal structure, and as they do not involve the movement of extended volumes of the material, they cannot either disturb or be disturbed by the conditions at the external boundary of the crystal. Further, the space-patterns of the characteristic vibrations of the lattice are prescribed by the crystal structure, the repetition units being either the same as the lattice spacings or integral multiples thereof. The assumption that the lattice vibrations have wave-lengths which are sub-multiples of an arbitrarily assumed external dimension of the crystal is therefore wholly inappropriate. For these reasons, the Born postulate cannot possibly represent the actual

state of affairs in a crystal. It is evident, in fact, that the Born theory is based on concepts derived from the macroscopic behaviour of elastic solids of the same kind as the theory of Debye which we have already examined and rejected. It follows that the Born crystal dynamics and its consequences must also be considered as unacceptable.

5. *The Spectroscopic Evidence*

It is an essential feature of both the Debye and Born theories that the vibration frequencies of a crystalline solid form a continuous spectrum. This is assumed *ab initio* in the Debye theory, while it follows as a necessary consequence of the postulate of the cyclic lattice on which the Born dynamics is based. The vibration spectrum in the Born theory is divided into the so-called acoustical and optical branches, but it would seem that this distinction does not correspond to any recognisable differences in spectral character. Both the acoustical and optical branches appear as continuous spectra, both have " transverse " and " longitudinal " frequencies, and they also overlap over extensive ranges of frequency. As a typical example illustrating the behaviour of crystals assumed in the Born theory, we may quote the calculations and graphical representations of the vibration spectrum of rock-salt contained in a recent paper by Kellermann (*Phil. Trans.*, May 1940). It will be seen that the features there shown stand in the sharpest contrast with those indicated by the theoretical considerations put forward in the present paper, namely that the infra-red and elastic vibration-spectra appear in quite different frequency ranges, that the infra-red spectrum consists entirely of discrete or monochromatic frequencies, while the elastic vibrations form a continuous spectrum.

Several experimental methods of studying the frequency spectrum of crystal lattices are available at the present time. A method applicable to all transparent crystals and covering the whole frequency range is the spectroscopic analysis of the scattered radiations emerging from a crystal when it is traversed by a beam of monochromatic light.* A striking and quite general feature emerging from such studies is the *sharpness* of the lines of displaced frequencey appearing in the spectra which represent the infra-red vibrations of the solid. These lines are usually quite as sharp as the lines of the incident radiation. This is the case both when the lines represent the extensional or distortional vibrations of the ions or molecules in the crystal lattice, as also when they represent translational or rotational movements. Vibrations of the latter kind which are usually of low frequency are specially

* This field of research is reviewed in an article in the *Journal of the Franklin Institute* for September 1941.

characteristic of the crystalline state. Even in those cases where such lines show an appreciable width at ordinary temperatures, they sharpen to the finest possible lines when the crystal is immersed in liquid air. Such lines fail to appear when the substance is in the amorphous or fluid state, being then replaced by diffuse continua, thus clearly showing that the monochromatism of the vibrations is a consequence of the regular lattice structure of the crystal. As examples proving that the behaviour of actual crystals bears no resemblance to that assumed in the Debye and Born theories, we may mention the cases of the elementary solids, *e.g.*, diamond, sulphur and white phosphorus, as also simple ionic structures, *e.g.*, rock-salt. Every one of these crystals shows well-defined lines in the spectrum of the light scattered by it.

The luminescence of crystals excited by light or by electronic bombardment is another avenue of approach to the study of their lattice spectra. In this case, the transitions between the infra-red energy levels occur in combination with the electronic transitions. The method is therefore applicable for the study of the lattice spectra only when the levels of the electronic transitions are sharply defined. To secure this result, it is usually necessary to cool the crystal to liquid air or even to liquid hydrogen temperature. The subsidiary bands arising from the combinations of the electronic with the infra-red transitions are then found to be quite sharp. Various cases of this kind may be mentioned, *e.g.*, the luminescence of crystals due to atoms of chromium or of the rare earths embedded in their lattices, and the luminescence of the uranyl salts. Recently, it has been found by Nayar working in the laboratory of this Institute that the luminescence of diamond is also resolvable into discrete frequencies at low temperatures, thus enabling its lattice spectrum to be determined. The evidence derived from all such studies points conclusively to the monochromatic nature of the infra-red vibrations characteristic of crystal lattices.

Thirdly, we may mention the avenue of approach to the study of the lattice vibrations provided by the absorption spectra in the visible and ultra-violet. This method is applicable both in the special cases of luminescent crystals and also more generally, *e.g.*, the coloured metallic salts, the salts of the rare earths and organic crystals. Here again, since the infra-red and electronic transitions appear in combination, it is necessary to cool the crystals down to liquid air or even liquid hydrogen temperature before definite information regarding the nature of the lattice spectra can be obtained. The experimental results in such cases as have been fully studied show clearly the monochromatic character of the infra-red vibrations.

Finally, it may be said that the results of infra-red spectroscopy do not contradict the conclusions arrived at by the different methods referred to

above. Much of our knowledge regarding the lattice frequencies of crystals is derived from observations of the reflecting power of crystals for infra-red radiations as a function of wave-length. It is obvious that this method, while yielding useful information, cannot be considered as a method of spectral analysis properly so-called, since the reflecting power does not vanish at frequencies other than those characteristic of the crystal. Absorption methods *using very thin plates* would evidently be more suitable, but such studies have not been very numerous.

6. *Lattice Frequencies and Superlattice Frequencies*

The theoretical considerations indicated earlier and the experimental results of spectroscopic research agree in showing that the vibrations of a crystal lattice which appear as monochromatic frequencies in the infra-red spectrum stand in a class apart from the elastic vibrations of macroscopic physics. In considering the relations between crystal properties and crystal structure, we would be justified in ignoring the vibrations of the macroscopic type, since the fraction of the total thermal energy which they carry is negligible. The atomic vibrations appearing in the infra-red spectrum may be classed as lattice vibrations and superlattice vibrations of different orders. The lattice vibrations are those possible when the unit cell of the crystal lattice is the repeating unit in the dynamic space pattern. The term also includes vibrations of the same or nearly the same frequency as the lattice vibrations which arise when superlattices of increasing size are considered as the repeating units. The superlattice frequencies are those which present themselves *only* when cells of superlattice size are considered. It is evident that they may be roughly pictured as due to the cells of the crystal lattice oscillating against each other in groups. Thus, if a cell of double size and therefore containing 8 lattice cells is the unit of the pattern, the superlattice frequencies of the first order would include 21 out of the 24 degrees of freedom of motion of these 8 cells, while the superlattice frequencies of all the higher orders together would carry only the 3 residual degrees of freedom. The successive orders would thus diminish rapidly in importance. *Pari passu*, their frequencies would diminish owing to the increasing mass of the oscillating units.

As explained above, the superlattice frequencies would be low and would lie in the remote infra-red region of the spectrum. Their contribution to the thermal energy would be small and of importance only at the lowest temperatures. They are, in fact, the nearest analogy in the present theory to the elastic vibrations of macroscopic physics, but differ from them in possessing specifiable frequencies instead of being merely segments in a continuous spectrum. *The existence of monochromatic superlattice frequencies*

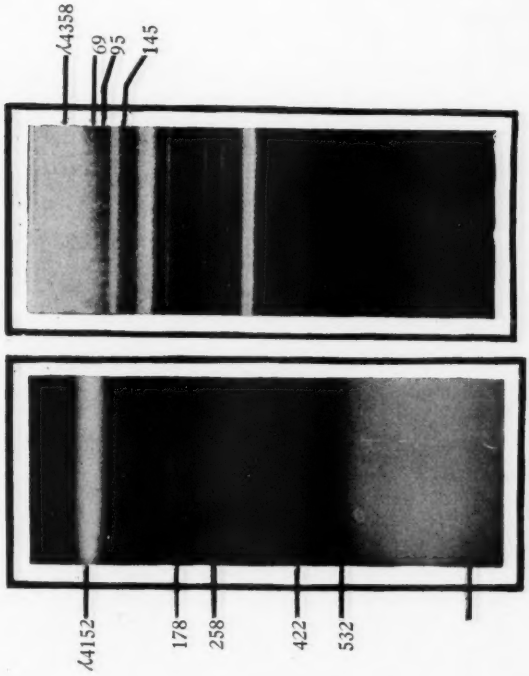

FIG. 1

FIG. 2

FIG. 1. Superlattice frequencies in quartz appearing in light-scattering

FIG. 2. Superlattice frequencies in diamond appearing in fluorescence

has been established by spectroscopic studies made at this Institute with diamond and quartz. These are shown in Figs. 1 and 2 in Plate XXXIV. That similar vibrations exist also in other crystals is hardly to be doubted, though lying in the remote infra-red, they would naturally be less easily demonstrable by spectroscopic investigation. In fact, specific heat determinations at the lowest temperatures are probably the easiest way in which their reality can, in general, be proved.

7. *The Specific Heat Data*

The present paper is followed by several others in which the experimental facts concerning the specific heats of various substances of simple composition are examined in detail. These papers speak for themselves. It is sufficient to remark that the results of the examination furnish the clearest experimental proof of the correctness of the new theoretical approach to the problem of the specific heats of solids indicated in the preceding pages.

8. *Summary*

The theory of the specific heats of crystals is considered in this paper from a new standpoint. A crystal being a regular periodic arrangement in space of material particles, the possible vibrations of the atoms in such a structure can be divided into two groups, namely those occurring in a macroscopic scale, and those fundamentally involving the crystal structure. The second group can be further subdivided into lattice vibrations and superlattice vibrations in which the modes of vibration form repeating patterns in space; the unit of this pattern is identical with the lattice cells in one case, and is an integral multiple of its size in the second case. It is shown that the part of the thermal energy associated with the macroscopic or elastic vibrations appearing as a continuous spectrum is entirely negligible. The bulk of the thermal energy is associated with the lattice frequencies properly so called which appear as monochromatic lines in the infra-red spectrum. The residue is associated with the superlattice frequencies of different orders which are also monochromatic. These frequencies appear in the remote infra-red region of the spectrum and their contribution to the specific heat is relatively important only at low temperatures. The spectroscopic evidence regarding crystals is reviewed and shown to be in full accord with these ideas. The specific heat theories of Debye and of Born are critically examined and it is shown that the assumptions on which they are based are theoretically unjustifiable, besides being in contradiction with the experimentally observed behaviour of crystals.

THE THERMAL ENERGY OF CRYSTALLINE SOLIDS : WHITE PHOSPHORUS

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

White phosphorus is an elementary solid which crystallises in the cubic system at ordinary temperatures. As its molecular and crystal structure is known, and its spectroscopic behaviour in the Raman effect has been the subject of detailed study, it becomes possible to offer a satisfactory interpretation of its specific heat data.

2. Molecular and Crystal Structure

Dumas (1826) determined the vapour density of phosphorus vapour and found the molecular formula to be P_4. Beckmann (1890) also found the molecular formula to be P_4 from the boiling point of a solution of phosphorus in CS_2 and this was confirmed by Hertz (1890) from the freezing point of a solution of phosphorus in benzene. Seyler (1884) had earlier arrived at the same conclusion from a consideration of the latent heat of fusion and the specific gravity of the solid and liquid at the melting point. Aston and Ramsay (1894) found that the P_4 formula also agrees with the observed surface tension of the molten liquid, while Smits and Bokhorst (1916) arrived at the same conclusion from the values of the critical constants. Stock and co-workers (1912), by studying the vapour density, found the molecule to continue as P_4 upto 700°, any dissociation that may occur taking place only at still higher temperatures. Bhagavantam (1930) has shown from the Raman effect data that the P_4 molecule must be tetrahedral in form and that the alternative configuration of a square is definitely excluded. The tetrahedral form of the P_4 molecule is confirmed by the study of electron diffraction by phosphorus vapour made by Maxwell, Hendrichs and Mosley (1935). Natta and Passerini (1930), as a result of X-ray investigation of phosphorus at $-35°$ C., came to the conclusion that white phosphorus belongs to the cubic system and has 4 P_4 molecules in the unit cell. At still lower temperatures, however, it ceases to be a cubic crystal.

3. Spectroscopic Data

Bhagavantam who was the first to study the Raman effect of white phosphorus reported the presence of only three frequencies at 374, 468 and 607 wave numbers, conforming to a tetrahedral model. Venkateswaran (1935) investigated this in greater detail by studying phosphorus in the solid, liquid and vapour states as well as also in solution, and found that a change of state has no marked effect on the Raman lines, except that the frequency at 603 increases by a few wave numbers in going from solid to liquid and from liquid to vapour states. He also made (1937) the important observation of the presence of a fairly sharp and intense line displaced by 36 wave numbers from the exciting radiation in the case of solid phosphorus. He calculated the frequency of vibration of the phosphorus molecules in the crystal lattice from Lindemann's modified formula to be $\Delta\nu = 27{\cdot}3$ cm.$^{-1}$ Bhagavantam and Venkatarayudu (1938) calculated the modes of vibration of the phosphorus molecule and obtained detailed expressions for the three frequencies by which they identified the 606 frequency to be due to the symmetrical vibration and hence single, 363 to be doubly degenerate and 465 to be triply degenerate, all the three being active in the Raman effect. This assignment is in agreement with the observations of Venkateswaran (1937) who had found that in the case of liquid phosphorus, the 606 line is strongly polarised while the other two are depolarised.

4. Calculation of the Specific Heat

Considering the 4 P_4 groups in the unit cell of the cubic crystal lattice, we have in all 48 degrees of freedom. The P_4 molecule itself has six internal vibrations, of which one is single, one is doubly and the other triply degenerate. Of the 48 degrees of freedom, 24 are thus identified with the three discrete Raman frequencies 363, 465 and 606 with their respective degeneracies. Amongst the remaining degrees of freedom, 12 must be identified with the three rotational oscillations (triply degenerate) of each of the four P_4 molecules in the unit cell. Since the P_4 molecule has tetrahedral symmetry and is located in a cubic cell, it would be optically isotropic and such rotational oscillations would therefore be inactive in the Raman effect. Hence, their frequency is not accessible to direct observation. Of the remaining 12 degrees of freedom, 3 must be identified with the linear translations of the unit cell as a whole. The remaining 9 degrees of freedom may therefore be assigned to the oscillations representing the "hindered translations" of the molecules within the cell. The low frequency line at 36 cm.$^{-1}$ observed by Venkateswaran in solid phosphorus may reasonably be identified with such translational oscillations of the molecules within the cell. This identification appears to be justified by the approximate agreement of this frequency with

that calculated from the Lindemann melting point formula. The alternative interpretation of the 36 cm.$^{-1}$ line as due to the rotational oscillation of the molecules is excluded, since such oscillation should be Raman inactive as already explained. Thus we see that of the 48 degrees of freedom of the unit cell, 45 degrees are identified with certain discrete frequencies and hence appear as Einstein terms in the expression for the specific heat of the phosphorus crystal.

The superlattice frequencies must be lower than the observed lowest frequency at 36 cm.$^{-1}$ which we have identified as that of translatory oscillation of the molecules. Since the data do not extend to very low temperatures, we shall take the superlattice frequency to be equal to 36 cm.$^{-1}$ itself. The frequency of the oscillation corresponding to " hindered rotations " of the P_4 molecules may be expected to be considerably higher. We shall take it as 67 cm.$^{-1}$ which is not unreasonably high and gives the best fit with the specific heat data. The gramme-molecular heat of solid phosphorus at temperature T may thus be written as

$$C_v = \left\{\frac{1}{4}\,E\left(\frac{\theta_{36}}{T}\right) + \frac{3}{4}\,E\left(\frac{\theta_{36}}{T}\right)\right\} + \left\{E\left(\frac{\theta_{67}}{T}\right)\right\} + \left\{\frac{1}{3}\,E\left(\frac{\theta_{603}}{T}\right) + \frac{2}{3}\,E\left(\frac{\theta_{363}}{T}\right) + E\left(\frac{\theta_{465}}{T}\right)\right\}.$$

The experimental data concerning specific heat of phosphorus at different temperatures are not available for the several discrete temperatures. However, we have mean specific heats observed between wide temperature intervals between four different temperature regions. These are between (1) 23° to 77°; (2) 82° to 194°; (3) 195° to 271°; and (4) 274° to 290° absolute. The first of these four determinations is due to Dewar (1913), while the other three are due to Ewald (1914). Hence, it will be necessary for comparing the calculated and observed values to calculate the molecular heat in a slightly different manner. Instead of calculating the derivatives of the corresponding energy functions with respect to temperature, we calculate the energy functions themselves. The total thermal energies at two different temperatures T_1 and T_2 being U_1 and U_2, the mean molecular heat between these two temperatures is

$$C_v = \frac{U_2 - U_1}{T_2 - T_1}.$$

The value of $(C_p - C_v)$ for phosphorus at the room temperature is calculated from the thermodynamic relation to be $= 3{\cdot}06$, while its values at the other mean temperatures are calculated with the aid of Grüneisen's law as was done by the author (1941) for the case of sulphur. The following table

TABLE

Specific Heat of Phosphorus

T° (Absolute)	$\frac{1}{4}$ $U_{E_{31}}$	$\frac{1}{4}$ $U_{E_{36}}$	$U_{E_{67}}$	Uinternal $= \frac{1}{3} U_{E_{603}} + \frac{2}{3} U_{E_{363}} + U_{E_{465}}$	Total U	Mean heat $C_v = \frac{U_2 - U_1}{T_2 - T_1}$	$C_p - C_v$	Total mean heat C_p calculated	Total mean heat C_p observed
23	9	27·36	8·9	= 0	45	9·45	0·1	9·55	9·60
77	80	241·5	230·2	(0·02+ 2·526+ 0·685)= 3·231	555				
82	87	262·92	256·6	(0·44+ 3·75 + 1·164)= 4·962	612	14·23	0·775	15·01	15·44
194	251	754·5	894·7	(19·79+153·6 +132)=305·39	2206				
195	253	760·5	898·56	(20·3 +156 +134·4)=310·7	2223	18·28	2·344	20·62	20·48
271	366	1099·5	1345	(72·9 +358 +371)=801·9	3612				
274	371	1113	1362	(75·6 +366·6 +382·3)=824·5	3670	19·63	3·06	22·69	22·0
290	395	1185	1456	(90·8 +415 +442·8)=948·6	3984				

compares the mean gramme-molecular heat of solid phosphorus thus calculated with the experimentally observed values.

It will be seen that the calculated values of the mean molecular heat of phosphorus agree well with the observed values.

In conclusion, the author desires to record his grateful thanks to Prof. Sir C. V. Raman, for his kind interest in this work.

5. *Summary*

The specific heat of solid phosphorus is calculated by considering the unit cell of 4 P_4 molecules. Of its total 48 degrees of freedom, 24 are identified with the internal vibrations of the P_4 molecule identified by their respective Raman frequencies with their appropriate degeneracies, 12 are associated with the inactive frequency of a triply degenerate rotational oscillation of each of the 4 P_4 molecules, 9 degrees of freedom with the observed low frequency vibration due to the " hindered translations " of the P_4 molecules in the unit cell. All these 45 terms being due to discrete frequencies, their Einstein terms are involved in the calculation of the specific heat. The remaining three degrees of freedom corresponding to the simple translations of the unit cell in the lattice are also assumed to contribute an Einstein term to the specific heat. The values thus calculated are in good agreement with the observed values.

REFERENCES

1. Aston and Ramsay .. *Jour. Chem. Soc.*, 1894, **65**, 167.
2. Beckmann .. *Z. Phys. Chem.*, 1890, **5**, 76.
3. Bhagavantam, S. .. *Ind. Jour. Phys.*, 1930, **5**, 39, 78.
4. Bhagavantam and Venkatarayudu, T. .. *Proc. Ind. Acad. Sci.*, 1938, **8**, 119.
5. Dewar, J. .. *Proc. Roy. Soc.*, A, 1913, **89**, 158.
6. Dumas .. *Ann. Chim. Phys.*, 1826, **33**, 341.
7. Ewald, R. .. *Ann. der Phys.*, 1914, **44**, 1215.
8. Hertz .. *Z. Phys. Chem.*, 1890, **6**, 358.
9. Maxwell, Hendricks and Mosley .. *Jour. Chem. Phys.*, 1935, **3**, 699.
10. Natta and Passerini .. *Nature*, 1930, **125**, 707.
11. Norris, R. .. *Proc. Ind. Acad. Sci.*, 1941, **13**, 291.
12. Seyler, C. A. .. *Chem. News*, 1884, **49**, 31.
13. Smits and Bokhorst .. *Z. Phys. Chem.*, 1916, **91**, 248.
14. Stock, Gibson and Stamm *Ber.*, 1912, **45**, 3527.
15. Venkateswaran, C. S. .. *Proc. Ind. Acad. Sci.*, 1935, **2**, 260; 1937, **4**, 345, 414.

THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: LITHIUM, TUNGSTEN, GOLD, SILICON AND GREY TIN

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1. Introduction

The success of Debye's formula in representing the variation with temperature of the specific heat of a large number of metals crystallizing in the cubic system has for many years been regarded as conclusive evidence for the correctness of the assumptions on which this theory is based. Gradually, however, various experimental facts have come to light which do not fit into the theory. According to Debye, the specific heat of an elementary solid is expressible as a function involving only one arbitrary constant known as the Debye characteristic temperature for the substance, this constant itself being expressible in terms of the elastic modulii of the solid. Several cases have however come to light in which it is impossible to fit the specific heat data into a formula of this kind. In order to preserve at least the framework of the theory, it has become the fashion to regard the " characteristic temperature " as being itself a function of the temperature and to exhibit its variation graphically. On a close examination of the matter, it is found that there are comparatively few cases in which the " Debye temperature " is even approximately constant over a wide range of temperature. Lead, calcium, molybdenum and vanadium are examples of cases in which a fairly satisfactory fit is obtained. On the other hand, there are equally numerous cases in which the " characteristic temperature " shows quite distinct variations, increasing with the temperature as is the case of gold, diminishing as in tungsten, and in other cases, again, showing more complicated types of variation. In the cases of lithium, grey tin and metallic silicon, the variations are so large that the Debye formula does not even roughly represent the specific heat curve.

An extensive literature has grown up in the attempt to interpret these failures of the Debye theory on the basis of special hypotheses. It is not proposed here to enter into that literature, as we shall consider the whole question from a more general point of view. Debye's identification of the possible atomic movements in a crystal with the elastic vibrations of a continuous solid seems justifiable only when the wave-length of such vibrations is

sufficiently large in comparison with the lattice spacings of the crystal. There appears, however, no reason for assuming that all the possible types of atomic movement can be described in this fashion. Indeed, wherever it has been possible to make a direct experimental study of the question, *e.g.*, by photographing the Raman spectra, it is found that such an assumption does not correctly represent the facts. The spectroscope, in fact, discloses that the atomic vibrations even in elementary solids, *viz.*, diamond, phosphorus and sulphur, exhibit numerous monochromatic frequencies, the position and number of which may be correlated with the crystal structure of the solid. Such methods of optical study are, unfortunately, not open to us in the case of metals. But we have no reason to suppose that a similar situation does not exist in their case as well. It may be recalled that in making the first attempt to develop a quantum theory of specific heats, Einstein (1907), assumed that the vibrations of the atoms in a solid are monochromatic. The difficulty felt by him later (1911) in sustaining this hypothesis, namely that the vibrations of an atom would be highly damped by its reactions with its neighbours, disappears when it is recalled that the characteristic vibrations of the lattice necessarily occur in the same way in all its cells and are therefore undamped. The highly monochromatic character of the frequencies usually exhibited by crystals in the Raman effect is, in fact, a complete vindication of Einstein's original hypothesis.

From the foregoing considerations, it is clear that for the evaluation of the specific heat, we have to find the frequencies of atomic vibration in the crystal and to assign to each such frequency an Einstein function with the appropriate weight factor. The principal Einstein terms relate to the frequencies of vibration in which the lattice cell is the repeating unit of the vibration pattern in space. Further terms would also have to be added to represent the superlattice frequencies for which the vibration pattern in space is a multiple of the size of the lattice cell, as explained more fully in papers by Sir C. V. Raman and Dr. C. S. Venkateswaran appearing in these *Proceedings*. The elastic vibrations of the solid properly so-called, however, make no sensible contribution to the thermal energy.

2. *Relation to Crystal Structure*

We may take the basis group in the cases now under consideration to be the unit cube. This contains two atoms in the case of body-centred lattices, four in the case of face-centred ones, and eight in diamond-like structures. The case of the body-centred lattice is the simplest of all. This may be considered as made up of two interpenetrating simple cubic lattices, one of which is formd by the corner atoms and the other by the central atom of the cube. The three translations of the cell as a whole involve three degrees of freedom.

The Einstein frequency would then correspond to the movement of one single cubic lattice against the other and because of the cubic symmetry, this must be triply degenerate. The case of a face-centred lattice is somewhat more complicated. There are four interpenetrating simple cubic lattices to be considered. Here as well, three degrees of freedom relate to the translation of the cell. The remaining nine degrees of freedom are associated with the possible modes of vibration of the four lattices against each other. Since each frequency must be triply degenerate, we are concerned with three Einstein frequencies. In the case of diamond-like lattices, the unit cell of eight atoms is made up of two groups of four each forming a face-centred cubic lattice. Assigning three degrees of freedom to the translations, twenty-one degrees of freedom are left over. There would then be, in general, seven triply degenerate Einstein frequencies.

The evaluation of the Einstein terms in the specific heat thus involves a knowledge of one characteristic frequency for body-centred lattices, three for face-centred ones, and seven for diamond-like structures. Provisionally and for the sake of simplicity, the three frequencies of a face-centred lattice may be replaced by a single representative frequency. In the case of diamond-like structures, the spectroscopic evidence afforded by diamond itself indicates that it is necessary to have at least two representative frequencies; one of these corresponds to an oscillation of the two face-centred cubic lattices against each other; the other frequency may be pictured as an oscillation of the component atoms in each such lattice amongst themselves. Of the total number of degrees of freedom, one half should evidently be assigned to the vibrations of the first type which would naturally have the higher frequency. Three degrees of freedom being assigned to the translations, the remainder are associated with the second and lower frequency.

The three degrees of translatory freedom of the unit cell appear in each case as superlattice frequencies. Taking a superlattice cell whose edge is double that of the unit cell, we assign three degrees of freedom to the translations of the enlarged cell and the remaining 21 degrees of freedom to seven triply degenerate superlattice frequencies. The three reserved degrees can then be passed on to superlattice frequencies of the second order, and so forth. For our present purpose, we may replace the seven superlattice frequencies of a particular order by a single representative frequency and also restrict ourselves to superlattice frequencies of the first two orders. The expressions for the specific heat accordingly reduce to

$$C_v = 3\,R\left[\frac{1}{2}\,E\left(\frac{h\nu_1}{kT}\right) + \frac{7}{16}\,E\left(\frac{h\nu_2}{kT}\right) + \frac{1}{16}\,E\left(\frac{h\nu_3}{kT}\right)\right]$$

for body-centred structures

$$C_v = 3R\left[\frac{3}{4}E\left(\frac{h\nu_1}{kT}\right) + \frac{7}{32}E\left(\frac{h\nu_2}{kT}\right) + \frac{1}{32}E\left(\frac{h\nu_3}{kT}\right)\right]$$

for face-centred structures

and $$C_v = 3R\left[\frac{1}{2}E\left(\frac{h\nu_1}{kT}\right) + \frac{3}{8}E\left(\frac{h\nu_2}{kT}\right) + \frac{7}{64}E\left(\frac{h\nu_3}{kT}\right) + \frac{1}{64}E\left(\frac{h\nu_4}{kT}\right)\right]$$

for diamond-like structures,

where E stands for Einstein function. The last two terms in each case refer to the superlattice frequencies of the first and second orders respectively.

Failing spectroscopic data, the frequencies can be evaluated from the specific heat data themselves. The superlattice frequency of the lowest order is obtained from the specific heat data at the lowest temperature where the contribution of other frequencies becomes negligible. Superlattice frequencies of other orders can similarly be found from the specific heat data at intermediate temperatures. The high-temperature specific heats where the contribution of superlattice vibrations is constant give the lattice frequencies. Towards the end of the paper we shall compare the lattice frequencies empirically found with those given by the melting point formula of Lindemann.

In the present paper the author has used the above method for calculating specific heats of several elements crystallizing in the cubic system which do not fit into the Debye theory. In other cases where the Debye theory gives an approximate fit with the experimental values, calculations show that it is always possible to express the specific heats slightly better by the new method. Such calculations have however, not been given here to save space.

3. *Specific Heats of Body-Centred Structures*

(*a*) *Lithium.*—Of all the metals having this structure, lithium is the most interesting since no single Debye function will fit the experimental results, the value of θ Debye changing from 328 at low temperatures to 430 at room temperatures. Various hypotheses have been suggested to explain this so-called anamoly, that given by Simon and Swain (1935) being the most discussed. They believe that Li ions are of two different kinds and some heat is taken up in changing one kind into another. The soundness of this assumption has been questioned and their value of θ Debye (510) is not supported by experimental evidence (Pankow, 1936). Fuch (1936) has tried to explain the specific heats on the assumption of anisotropy, but the values of θ Debye calculated by him on that basis show an even larger deviation than is experimentally the case. The values of the specific heat calculated by us (given below), however, are very close to the experimental values at all temperatures. It is noteworthy also that our Einstein frequency comes very close to that given by Lindemann's melting point formula.

The values of C_v have been taken from the paper by Simon and Swain (*loc. cit*). Beutler and Levis' (1934) results have not been used because the accuracy claimed by them is not very high, only the first place of decimals being shown.

TABLE I

Specific Heats of Li in Cals./deg. gm. atom

$\nu_1 = 8{\cdot}4 \times 10^{12}$, $\nu_2 = 4{\cdot}64 \times 10^{12}$, $\nu_3 = 1{\cdot}84 \times 10^{12}$

Experimental Data of Simon and Swain (1935)

Absolute temperature	Einstein contribution ν_1	Einstein contribution ν_2 and ν_3	Calculated C_v	Observed C_v	Difference observed −calculated	Debye function $\theta = 350$	Difference observed C_v −Debye C_v
15	..	·0364	·0364	·045	+·009	·037	+·008
20	..	·095	·095	·095	±·000	·087	+·008
25	..	·173	·173	·169	−·004	·169	±·000
30	·001	·278	·279	·273	−·006	·289	−·016
35	·0046	·4112	·416	·413	−·003	·452	−·039
40	·0133	·567	·580	·573	−·007	·652	−·079
45	·0327	·7376	·770	·770	±·000	·884	−·114
50	·064	·910	·974	·995	+·021	1·137	−·142
60	·169	1·239	1·41	1·42	+·01	1·67	−·45
70	·324	1·525	1·85	1·87	+·02	2·197	−·327
80	·509	1·757	2·27	2·31	+·04	2·67	−·36
90	·71	1·948	2·66	2·67	+·01	3·09	−·42
100	·906	2·104	3·01	3·02	+·01	3·46	−·44
110	1·093	2·228	3·32	3·32	±·000	3·77	−·45
120	1·269	2·330	3·60	3·59	−·01	4·02	−·43
140	1·569	2·479	4·05	4·01	−·04	4·45	−·44
160	1·813	2·586	4·40	4·34	−·06	4·75	−·41
180	2·006	2·656	4·66	4·57	−·09	4·98	−·42
200	2·156	2·724	4·88	4·78	−·10	5·14	−·36
240	2·372	2·793	5·17	5·28	+·11	5·36	−·08
280	2·518	2·844	5·36	5·31	−·05	5·52	−·21
300	2·575	2·860	5·44	5·39	−·05	5·63	−·24

(*b*) *Tungsten*.—This is the only metal for which the frequency spectrum has been worked out on the Born-Karman model (Fine, 1939). An approximate method which involved a solution of 140 cubic equations and in which the interaction of an atom and its fourteen neighbours only was considered, was used. The values calculated on that basis do not however show any distinct improvement on those calculated by Debye's formula for $\theta = 310$.

The agreement of the calculated values with Lange's data is excellent. The small deviations with respect to Zwikker's data are well within the experimental errors. This is shown by the considerable differences between the two series of measurements made by him in the region of temperatures given below.

TABLE II

Specific Heats of W in Cals./deg. gm. atom

$\nu_1 = 5{\cdot}4 \times 10^{12}$, $\nu_2 = 4{\cdot}48 \times 10^{12}$, $\nu_3 = 1{\cdot}67 \times 10^{12}$

Experimental Data of Lange (1924) *from* 26–91° A *and Zwikker* (1929) *from* 100–300° A

Absolute temperature	Einstein contribution ν_1	Einstein contribution ν_2 and ν_3	Calculated C_v	Observed C_v	Difference observed −calculated	Debye function $\theta = 310$	Difference observed C_v −Debye C_v
26·01	·013	·224	·237	·213	−·024	·272	−·059
32·3	·0617	·387	·449	·434	−·015	·506	−·072
38·8	·165	·587	·752	·750	−·002	·826	−·076
46·7	·355	·866	1·22	1·21	−·01	1·28	−·07
54·7	·592	1·144	1·74	1·80	+·06	1·77	+·03
74·4	1·176	1·701	2·88	2·87	−·01	2·85	−·02
78·3	1·272	1·797	3·07	3·07	±·00	3·03	+·04
84·2	1·42	1·908	3·33	3·33	±·00	3·29	+·04
91·1	1·576	2·026	3·60	3·60	±·00	3·55	+·05
100	1·745	2·156	3·90	3·77	−·13	3·85	+·08
200	2·592	2·741	5·33	5·30	−·03	5·30	±·00
300	2·796	2·869	5·67	5·87	+·20	5·65	+·22

4. *Specific Heats of a Face-Centred Structure*

Gold.—The specific heats of this metal have been measured by Clusius and Harteck (1928) and unlike most other metals of this structure are not expressed by one Debye function. The values of θ Debye vary between 160 and 186.

TABLE III

Specific Heats of Gold in Cals./deg. gm. atom

$\nu_1 = 3{\cdot}14 \times 10^{12}$, $\nu_2 = 1{\cdot}80 \times 10^{12}$, $\nu_3 = 1{\cdot}15 \times 10^{12}$

$C_p - C_v = 2{\cdot}09 \times 10^{-5}\, C_p\, T$

Experimental Data of Clusius and Harteck (1928)

Absolute temperature	Einstein contribution ν_2 and ν_3	Einstein contribution ν_1	Calculated C_v	Observed C_v	Difference observed −calculated	Debye function $\theta = 163$	Difference observed C_v −Debye C_v
14·96	·351	·0195	·371	·357	−·014	·354	+·003
15·73	·389	·029	·418	·431	+·013	·408	+·023
20·33	·618	·158	·776	·782	+·006	·816	−·024
24·9	·8057	·3945	1·200	1·252	+·052	1·32	−·068
32·5	1·0461	·9575	2·004	1·998	−·006	2·184	−·186
44	1·207	1·840	3·047	3·034	−·013	3·27	−·236
63·6	1·3243	2·8642	4·189	4·144	−·045	4·39	−·246
82·5	1·400	3·414	4·814	4·706	−·108	4·938	−·232
105	1·434	3·759	5·193	5·128	−·065	5·158	−·030
147·5	1·460	4·101	5·561	5·578	+·017	5·604	−·026
176·5	1·468	4·206	5·674	5·706	+·032	5·71	−·004
212·5	1·476	4·283	5·759	5·762	+·003	5·782	−·02

The deviations of the calculated values from the observed data are smaller than those of the Debye function and are not, as is the case with the latter in the same direction throughout. They are however larger than those observed with the body-centred structures. This is possibly due to the fact that we have taken a single Einstein frequency as a representative of a group of three, which may be different from one another.

5. *Specific Heats of Diamond-like Structures*

(*a*) *Metallic Silicon.*—Specific heats of this substance have been measured at six temperatures by Nernst and Schwers (1930) (20-90)° K, by Anderson (1930) (61–296)° K, and by Magnus (1923) (138–1000)° K. The Debye characteristic temperatures necessary to explain these results vary between 440 and 715. Nernst and Schwers' values are considerably (2–30)% lower than those extrapolated by Anderson from his own data. We have used the latter's extrapolated values in Table IV. C_p–C_v has been calculated by the usual formula from the compressibility ($\cdot 325 \times 10^{-12}$), linear coefficient of expansion ($7 \cdot 15 \times 10^{-6}$) and C_p at 296 (4·652), the former two being taken from the *International Critical Tables.*

With reference to the distinctly noticeable deviation at 296·3°K, it must be pointed out that Anderson does not claim a very high degree of accuracy for his work. The observed values of specific heats deviate considerably from those given by his curve in this region of temperature. Similar deviations take place at very low temperatures. The order of error can be judged from the fact that the specific heat given by him by interpolation at 65·6° K is ·920, while his own determination at a slightly lower temperature (65·1) is ·974. The small deviations from Magnus' data are not unexpected, since his values differ by about 4% from Anderson's at the temperatures 297 and 296·3° nearly common to both sets of observations.

(*b*) *Grey Tin.*—The calculation of $C_p - C_v$ requires the exact knowledge of the specific heat, compressibility, coefficient of expansion and density at one and the same temperature. For grey tin only the density and the mean coefficient of expansion between –163 and 18° C. are known. We have therefore calculated the values of $C\rho - C_v$ by an approximate formula of Grüneisen $\frac{C_p}{C_v} = 1 + 2\gamma T$, where γ is the coefficient of expansion, on the supposition that the coefficient of expansion is the same at all temperatures. γ is taken as $1 \cdot 59 \times 10^{-6}$.

The specific heats were expressed by Lange (1924) by two Debye functions $\frac{3}{4}$ Debye 280 + $\frac{1}{4}$ Debye 76. In terms of one Debye function the θ Debye ranges from (140–225)° K.

TABLE IV

Specific Heats of Metallic Silicon in Cals./deg. gm. atom

$\nu_1 = 14{\cdot}7 \times 10^{12}$, $\nu_2 = 6{\cdot}59 \times 10^{12}$, $\nu_3 = 3{\cdot}66 \times 10^{12}$, $\nu_4 = 1{\cdot}30 \times 10^{12}$

$C_p - C_v = 1{\cdot}84 \times 10^{-5} C_p{}^2 T$.

Experimental Data Extrapolated from Anderson (20·1 – 89·8) *Anderson*) 89·8 – 296·3), *Magnus* (350–1000)

Absolute temperature	Einstein contribution ν_3 and ν_4	Einstein contribution $\frac{9}{8}$ RE $\left(\frac{315}{T}\right)$	Einstein contribution $\frac{12}{8}$ RE $\left(\frac{705}{T}\right)$	Calculated C_v	Observed C_v	Difference observed −calculated	Debye function $\theta = 440$	Difference observed C_v −Debye C_v
20·1	·0527	..	..	·0527	·042	−·0107	·044	−·002
28·2	·1174	·0038	..	·121	·123	+·002	·122	+·001
39·7	·2351	·0506	..	·286	·336	+·050	·336	±·000
53·1	·3650	·210	·0009	·576	·630	+·054	·752	−·122
65·6	·4575	·4305	·0076	·896	·920	+·024	1·255	−·335
89·8	·5682	·8741	·073	1·515	1·495	−·02	2·27	−·775
98·8	·5932	1·0178	·1205	1·731	1·695	−·036	2·61	−·915
116·7	·6327	1·2573	·2605	2·151	2·152	+·001	3·207	−1·055
145·5	·6690	1·5506	·5845	2·804	2·740	−·064	3·97	−1·23
158·8	·6826	1·6271	·7095	3·019	2·993	−·016	4·18	−1·187
165·8	·6864	1·667	·7875	3·141	3·156	+·015	4·29	−1·134
186·9	·6976	1·7696	1·0225	3·490	3·496	+·006	4·58	−1·1084
199·2	·7032	1·821	1·1485	3·673	3·684	+·011	4·73	−1·046
213·6	·7085	1·8709	1·289	3·868	3·841	−·027	4·866	−1·025
237·5	·7150	1·9313	1·497	4·143	4·076	−·067	5·05	− ·974
253·3	·7187	1·9654	1·6225	4·307	4·335	+·028	5·144	− ·809
283·3	·7236	2·0209	1·820	4·565	4·566	+·001	5·30	− ·734
296·3	·7258	2·0378	1·896	4·660	4·534	−·126	5·347	− ·813
350	·7308	2·088	2·1445	4·963	4·972	+·009	5·525	− ·553
500	·7380	2·1603	2·5295	5·428	5·298	−·130	5·73	− ·432
700	·7408	2·071	2·738	5·550	5·558	+·008	5·835	− ·277
1000	·7423	2·214	2·8556	5·808	5·622	+·186	5·898	− ·276

TABLE V

Specific Heats of Grey Tin in Cals./deg. gm. atom

$\nu_1 = 5{\cdot}44 \times 10^{12}$, $\nu_2 = 2{\cdot}20 \times 10^{12}$, $\nu_3 = \nu_4 = 0{\cdot}77 \times 10^{12}$

Experimental Data of Lange (1924)

Absolute temperature	Einstein contribution ν_3 and ν_4	Einstein contribution $\frac{9}{8}$ RE $\left(\frac{105}{T}\right)$	Einstein contribution $\frac{12}{8}$ E $\left(\frac{260}{T}\right)$	Calculated C_v	Observed C_v	Difference observed −calculated C	Debye function $\theta = 140$	Difference observed C_v −Debye C_v
15·5	·471	·1168	..	·588	·599	+·011	·599	± ·000
18·2	·534	·2335	..	·768	·755	−·013	·909	− ·154
22·35	·5899	·4568	·004	1·051	1·056	+·005	1·45	− ·394
26·8	·6367	·7088	·017	1·363	1·375	+·009	2·04	− ·665
31·5	·6645	·9488	·053	1·666	1·675	+·009	2·63	− ·955
37·3	·6864	1·1966	·136	2·019	2·00	−·019	3·23	−1·23
44·9	·704	1·443	·307	2·45	2·36	−·09	3·83	−1·47
52·3	·714	1·612	·518	2·84	2·80	−·04	4·27	−1·37
59·3	·721	1·731	·734	3·19	3·14	−·05	4·58	−1·44
69·5	·727	1·850	1·039	3·62	3·67	+·05	4·91	−1·24
92·5	·735	2·007	1·602	4·34	4·42	+·08	5·33	− ·91
102·6	·737	2·05	1·799	4·59	4·73	+·14	5·44	− ·71
283·6	·743	2·208	2·776	5·72	6·08	+·36	5·88	+ ·20

6. *Remarks on the Frequencies Assumed*

In Table VI the values of the lattice frequencies obtained from the specific heat data are compared with those deduced from the Lindemann melting point formula. The following form given by Grüneisen in his article in the " Handbuch der Physik " has been used

$$\nu = 2{\cdot}5 \times 10^{12} \sqrt{\frac{T_s}{AV_0^{2/3}}}$$

where T_s = melting point in absolute degrees, A = atomic weight and V_o = atomic volume.

TABLE VI

Comparison of Frequencies

Substance	ν from Lindemann formula		Einstein ν from specific heat data	
	ν	$\theta = \frac{h\nu}{K}$	ν	$\theta = \frac{h\nu}{K}$
		deg. K		deg. K
Lithium	$8{\cdot}7 \times 10^{12}$	417	$8{\cdot}4 \times 10^{12}$	400
Tungsten	$5{\cdot}23 \times 10^{12}$	253	$5{\cdot}4 \times 10^{12}$	260
Gold	$3{\cdot}34 \times 10^{12}$	160	$3{\cdot}14 \times 10^{12}$	350
Silicon	$8{\cdot}51 \times 10^{12}$	407	$6{\cdot}59 \times 10^{12}$	315
			$14{\cdot}7 \times 10^{12}$	705
Grey tin	$1{\cdot}86 \times 10^{12}$*	89*	$2{\cdot}20 \times 10^{12}$	105
			$5{\cdot}44 \times 10^{12}$	260

* From data for ordinary tin.

For the first three metals the frequencies obtained from Lindemann formula are very near to those used by us. In the latter two cases such agreement is not to be expected because two frequencies are involved. The lower of the two frequencies, however, comes near the Lindemann frequency. It is noteworthy that, as in the case of diamond, one frequency is about double the other.

An independent estimate of the higher frequency of silicon can be made by the use of Nagendra Nath's theory of the vibrations of the diamond lattice (1934). His formula for the higher frequency 1332 cm.$^{-1}$ of diamond is

$$\nu = \frac{1}{2\pi c} \sqrt{\left[\frac{8}{3M}\left(K + 8\,\frac{K' - K'''}{p^2}\right)\right]}$$

which must also hold good for silicon because of the similarity of structure. K, K′ and K‴ in the formula stand for the force constants for primary valence, directed valence and intravalence, respectively, while M is the mass of the atom and p the distance between any two connected atoms. The second term in the above formula is unknown for silicon but is comparatively small (about 30% of the first) for the force constants used by Nagendra Nath for carbon. The value of K for silicon has been found to be $1{\cdot}7 \times 10^5$ dynes/cm.

by Still and Yost (1937) from the Raman spectrum of disilane. The corresponding value of K for carbon from a compound of similar structure is $4{\cdot}64 \times 10^5$ dynes/cm. If the latter value is put in the above formula for diamond, the first term by itself (neglecting the other) gives the frequency as 1308 cm.$^{-1}$ which is near the observed value. We shall therefore not be far wrong in calculating the frequency for silicon in the same way from the value K and neglecting $\left(\frac{K' - K'''}{p^2}\right)$. The frequency thus obtained is 516 cm.$^{-1}$ which is not so different from the 491 cm.$^{-1}$ adopted for the specific heat calculations. An alternative method of calculation is to assume that

$$\frac{\nu \text{ silicon}}{\nu \text{ carbon}} = \sqrt{\frac{M_{carbon} \times K_{si}}{M_{si} \times K_{carbon}}} = \frac{\nu_{si}}{1332}$$

which gives us 525 cm.$^{-1}$ for ν_{si} on using the values of K quoted above.

In conclusion the author wishes to thank Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his guidance and encouragement.

7. *Summary*

It is shown in the paper that the specific heat formula for all metals must necessarily include two types of Einstein terms, one corresponding to the lattice frequencies and the other to the superlattice frequencies. The number of lattice frequencies is shown to be one in the case of body-centred cubic lattices, three in the case of face-centred cubic types and seven in diamond-like structures. In the latter two cases the groups of frequencies have been replaced for simplicity by one and two representative frequencies respectively. The specific heats of the so-called anomalous cases, Li, W, Au, Si and grey tin have been calculated on the above basis and a satisfactory agreement with experimental results has been obtained. In the first two types of structures the monochromatic lattice frequencies obtained are shown to be of the same order as those given by Lindemann's melting point formula.

REFERENCES

Einstein	.. *Annalen der Physik.*, 1907, **22,** 180, 800.
————	.. *Ibid.*, 1911, **35,** 679.
Simon and Swain	.. *Zs. f. Phys. Chemie*, 1935, **28B,** 189.
Pankow	.. *Helv. Phys. Acta*, 1936, **9,** 87.
Fuch	.. *Proc. Roy. Soc.*, 1936, **157 A,** 444.
Beutler and Levi	.. *Zs. f. Phys. Chemie*, 1934, **B 24,** 278.
Fine	.. *Physical Review*, 1939, **56,** 358.
Lange	.. *Zs. f. Phys. Chemie*, 1924, **110,** 343.
Zwikker	.. *Zeits. f. Physik*, 1929, **52,** 668.
Clusius and Harteck	.. *Zs. f. Phys. Chemie*, 1928, **134,** 243.
Nernst and Schwers	.. *Preuss. Akad. wissen Berl.*, 1914, **10,** 355.
Anderson	.. *J. Am. Chem. Soc.*, 1930, **52,** 2301.
Magnus	.. *Annalen d. Physik*, 1923, **70,** 325.
Grüneisen	.. *Handbuch der Physik*, 1926, **10,** 52.
Nagendra Nath	.. *Proc. Ind. Acad. Sci.*, 1934, **1,** 343.
Still and Yost	.. *J. Chem. Phys.*, 1937, 5, 94.

THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: DIAMOND

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1. Introduction

Diamond is the outstanding example of an elementary substance in the solid state which shows an abnormally low specific heat at ordinary temperatures rising to the normal value at very high temperatures. The measurements of specific heat by Weber (1875) made with diamond exhibiting this phenomenon enabled Einstein (1907) to make a test of the quantum theory of specific heats in his first classic paper on the subject. Later determinations by Dewar (1905) and by Nernst (1911) showed that the specific heat of diamond tends to zero at very low temperatures. These measurements furnished material for a test of the formulæ for specific heat proposed by Nernst and Lindemann (1911) and by Debye (1912). It should be noted that these early theories and discussions were based upon postulates regarding the nature of the vibration spectrum of diamond and not upon any independently ascertained facts regarding the latter. Of late years, however, investigations on the Raman effect, on infra-red absorption and especially the recent studies of Nayar (1941) on the absorption of ultra-violet radiations and the luminescence spectrum of diamond have furnished us with a wealth of information regarding the the lattice spectrum of this crystal. The information thus derived definitely contradicts the assumption of Debye that the lattice frequencies of diamond form a continuous spectrum of elastic vibrations bounded by an upper limiting frequency. The actual nature of the vibrations should obviously stand in the closest relation to the crystal structure of diamond. Some light has been thrown on the subject by the investigation of Nagendra Nath (1934) and of Venkatarayudu (1938). Accurate data for the specific heat are also forthcoming from the work of Magnus and Hodler (1926) and especially of Pitzer (1938) over a wide range of temperatures. The time is thus ripe for an attempt to consider the thermal energy data for diamond on a new basis, namely the spectroscopic facts on the one hand and the known crystal structure with its possible modes of vibration, on the other.

2. Experimental Data for Specific Heat

Following the early work of Regnault, Wullner and Bettendorf and De La Rive and Marcet indicating that the specific heat of diamond

increases with the rise of temperature, Weber (*loc. cit.*) studied such variation over a large range of temperature.

Magnus and Hodler (1926) determined the specific heat of diamond at high temperatures. More recently Pitzer (1938) has measured the specific heat of diamond over the temperature range 70° K.—300° K. He took twenty grams of diamonds of a grade known as " bortz ". Their heat capacity was believed to be the same as that of perfect diamonds within the limits of observational error. Pitzer points out that the data of Nernst below 100° K. are not very reliable. According to Pitzer himself, the error in his results may be as large as 5% at the lowest temperatures where the heat capacity of the diamonds was only about one-tenth of the heat capacity of the empty calorimeter, but it rapidly diminishes to about 0·2% at 150° K. At the highest temperatures the errors are somewhat larger on account of the rapid heat exchange by radiation.

Robertson, Fox and Martin (1934) drew attention to the fact that there are apparently two types of diamond which differ in their spectroscopic behaviour, and (1936) determined the specific heats of the two types to see if they were different. They concluded from their researches that the specific heats were the same within the limits of experimental error.

The values given in the *International Critical Tables* (1926 edition) for the atomic heat at low temperatures are indicated therein to be very uncertain, and it is mentioned that for high temperatures the (recent) data of Magnus and Hodler should be referred to. We shall therefore regard as standard Pitzer's values between 70° K. and 288° K: and Magnus and Hodler's values for the higher temperatures. These values are shown in Table I.

3. *Raman Effect and Infra-Red Absorption*

Raman Effect Data.—Ramaswamy (1930), as also Robertson and Fox (1930), discovered that diamond exhibits in the Raman effect a spectrum line with a frequency shift of 1332 cm.$^{-1}$ This is so intense that it can be photographed even with a tiny diamond with an exposure of an hour or two. Bhagavantam (1930), who investigated the subject with special thoroughness, found in addition to this intense line, others of very low intensity lying on either side of it. Of these again, the most prominent is the one having the smallest frequency shift, namely 1158 cm.$^{-1}$ The other lines having frequency shifts of 1288, 1382, 1431, 1480 and 1585 cm.$^{-1}$ are much weaker, and require large clear diamonds and long exposures to enable them to be recorded. Robertson, Fox and Martin (1934) established that the Raman frequency of 1332 cm.$^{-1}$ is the same for diamonds of the two types studied by them. Nayar (1941) has studied the temperature variation of the principal Raman

frequency 1332 cm.$^{-1}$ At liquid air temperature, the frequency shift is 1333·8 cm.$^{-1}$, at the room temperature 1332·1 cm.$^{-1}$, at 182° C. it is 1331·0 cm.$^{-1}$ while at 857° C. this is 1316·4 cm.$^{-1}$

Infra-red Absorption.— The infra-red spectrum of diamond has been studied by Angstrom, Julius, Reinkober (1911) and recently by Robertson, Fox and Martin (1934). From the selection rules due to Placzek for the lattice vibrations in cubic crystals, it follows that vibrations which are active in the Raman effect should be inactive in the infra-red, and *vice versa.* Hence it follows that the Raman frequency 1332 cm.$^{-1}$ should not be observable in infra-red absorption. Actually, however, diamonds of type I exhibit a strong absorption in this region, and it is seen from the data reproduced in the paper of Robertson *et al.*, that the curve exhibits a very steep fall or edge coinciding with 1332 cm.$^{-1}$, that is, with the Raman line. It is therefore evident that the observed absorption is due to the same lattice vibration which gives rise to the Raman-active frequency 1332 cm.$^{-1}$ which for some reason (not yet fully understood) is also active in infra-red absorption. Diamonds of type II, according to Robsertson *et al.*, do not show this strong absorption at 1332 wave-numbers. Reinkober's curve for such a diamond, however, exhibits a series of small undulations which correspond more or less exactly with the Raman frequencies of diamond noticed by Bhagavantam (*loc. cit.*), including especially the principal frequency at 1332 cm.$^{-1}$ Reinkober also noticed a weak but significant infra-red absorption at 710 cm.$^{-1}$ the limit of which is at 760 cm.$^{-1}$ As no corresponding line is observed in light scattering, it is to be presumed that this is a lattice oscillation which is normally inactive both in light scattering and in infra-red absorption.

4. Luminescence and Ultra-Violet Absorption

The fluorescence and ultra-violet absorption spectra of numerous diamonds have been recently investigated by Nayar (1941) both at room and liquid air temperatures with very interesting results. He finds that all diamonds exhibit an electronic band which becomes very sharp at liquid air temperature, then appearing at 4153 A.U. This is seen as a dark line in absorption and as a bright line both in fluorescence and phosphorescence. As a result of combination between this electronic vibration and the lattice vibrations in the crystal, new bands arise which appear with increased frequencies in absorption and with diminished frequencies in luminescence. The differences between the electronic frequency and these subsidiary absorption and emission frequencies enable us to evaluate the lattice frequencies of diamond. Of these bands, by far the most intense are two, shifted from the position of the electronic band by 780 cm.$^{-1}$ and 1332 cm.$^{-1}$ respectively. These are accompanied by fainter companions adjacent to them with smaller

frequency shifts. The other bands of higher frequencies are very weak and diffuse and may be explained as overtones and combinations. As has been pointed out by Nayar, there is a general correspondence between the lattice frequencies deduced from ultra-violet absorption and luminescence data and from the Raman effect results on the one hand and the infra-red absorption on the other. We are thus clearly justified by the spectroscopic data in assuming that the fundamental lattice vibrations in diamond fall into two groups with representative frequencies 1332 cm.$^{-1}$ and 780 cm.$^{-1}$ respectively.

5. Vibrations of the Diamond Lattice

The diamond lattice, as is well known, consists of two interpenetrating cubic face-centred lattices, in which each of the carbon atoms belonging to one lattice is bound to its four nearest neighbours in the other lattice at the tetrahedral valence angles. We can recognize in this structure cubic cells with edges 3·561 Å having four atoms within the cell, six at the centres of the faces and eight atoms at the corners. The eight corner atoms are equivalent to one atom, the six face-centre atoms to three, which with the four atoms inside make eight atoms per unit cell. Of these, the four belonging to one lattice lie within the cell and the remaining four are shared with the neighbouring cells.

The possible modes of vibration of the diamond lattice may be looked at from two entirely distinct points of view. The first would be to ignore the crystalline structure, and following Debye to treat diamond as a continuum traversed by longitudinal and transverse waves. This idea of the continuum would be appropriate only so long as the wave-length of the acoustic waves is many times greater than the largest atomic spacings of the crystal. The considerations of Debye, however, cease to represent the position even approximately when the wave-length of the oscillations considered is not greater than four times the atomic spacing. Vibrations of higher frequencies should be pictured in quite a different way.

Considering the 8 atoms in the cubic cell, we can imagine these to oscillate against each other in such manner that their centre of gravity remains at rest, it being further assumed that the corresponding atoms in all the cells oscillate with the same frequency and phase. Nagendra Nath (1934) has discussed and evaluated the frequency of a particularly simple type of vibration, namely that in which the two interpenetrating face-centred cubic lattices forming the diamond structure oscillate with respect to each other as rigid wholes. He has shown that such a vibration can be identified with that giving rise to the Raman line 1332 cm.$^{-1}$ The expression for the frequency of this line obtained by him may be put in the form

$$\nu = \frac{1}{2\pi}\sqrt{\frac{8}{3M}\,(K + 8K_a)}, \qquad (1)$$

where M is the mass of the carbon atom and K, K_α are force constants denoting primary valence (four nearest atoms) and directed valence respectively. If we give reasonable values to K and K_α, the frequency turns out to be of the same order as the observed Raman frequency of 1332 wave-numbers. Venkatrayudu (1938) has shown on the group theory that such an oscillation of the interpenetrating lattices should be active in the Raman effect.

Regarding the two interpenetrating face-centred cubic lattices as single units oscillating against each other, it would follow that such oscillation being triply degenerate would represent three out of the six degrees of freedom of such a system. We may therefore assign half the total number of degrees of freedom in the crystal to the group of frequencies of which 1332 $cm.^{-1}$ is regarded as representative. The degrees of freedom associated with each unit cell being twenty-four, twelve are thus attached to the 1332 $cm.^{-1}$ group of frequencies. The three degrees of freedom of translation of the unit cell would be associated with the superlattice frequencies. Nine degrees of freedom would thus be left over for the group of vibrations of which 780 $cm.^{-1}$ is representative. It is worthy of remark that this division of 24 degrees of freedom into 12, 9 and 3 runs parallel to the division of the 8 atoms of the cell into 4, 3 and 1 respectively within the cell, at the face-centres and at the corners. The vibrations of frequency 780 $cm.^{-1}$ are no doubt to be described as oscillations of the atoms in each face-centred lattice amongst themselves.

6. *Superlattice Frequencies*

It now remains to associate the superlattice frequencies with the three translations of the unit cell in the crystal. The fluorescence and absorption spectra studied by Nayar exhibit other features besides the intense bands having their heads at 1332 and 780 wave-numbers which we have taken to be representative of the lattice frequencies. Most noticeable amongst these other features is a fairly bright band sharply limited at 532 wave-numbers, and followed by a succession of fainter bands. We shall take the frequency of 532 wave-numbers as representative of the superlattice frequencies of the first order. Nayar's plates also show two feeble bands of approximately equal intensity displaced by 178 and 258 wave-numbers respectively from the electronic band. We shall take the mean of the two, namely 218 as representing the superlattice frequencies of the second order. Of the 24 degrees of freedom of translation of the 8 cells included in the superlattice, 21 are associated with the first order and 3 with the second order. The atomic heat C_v of diamond is accordingly expressed by the formula

$$C_v = \frac{3R}{8}\left[4E\left(\frac{h\nu_1}{kT}\right) + 3E\left(\frac{h\nu_2}{kT}\right) + \frac{7}{8}E\left(\frac{h\nu_3}{kT}\right) + \frac{1}{8}E\left(\frac{h\nu_4}{kT}\right)\right] \qquad (2)$$

where ν_1, ν_2, ν_3, ν_4 are respectively 1332, 780, 532 and 218 in spectroscopic units. Here, E denotes the Einstein function, R is the gas constant, h and k are Planck's constant and Boltzmann's constant respectively. The values calculated from relation (2) have been given in Table I.

To compare the calculated values of C_v with the accepted experimental values of C_p, we have to subtract from the observed values the difference $(C_p - C_v)$. In the case of Pitzer's data this amounts to 0·001 cal./ °C. in the last four observations, the difference being even less at lower temperatures. This correction has been made in the values given in the table. Magnus and Hodler have corrected their own data and the values of C_v as given by them, have been reproduced in the table.

TABLE I

Comparison of the Calculated and the Experimental Values

Temp. °K.	C_v CALCULATED		C_v Observed	Temp. °K.	C_v CALCULATED		C_v Observed
	Debye's Formula $\nu_m = 1332$ cm.$^{-1}$	Spectroscopic data			Debye's Formula $\nu_m = 1332$ cm.$^{-1}$	Spectroscopic data	
70·16	·023	·022	·022	276·6	1·179	1·247	1·256
75·37	·029	·029	·030	288·0	1·289	1·355	1·354
81·59	·036	·036	·036				
88·65	·047	·046	·045	273	1·143	1·215	1·252
96·68	·061	·059	·059	300	1·405	1·469	1·520
105·1	·078	·082	·079	350	1·898	1·931	1·985
113·0	·096	·097	·099	400	2·362	2·366	2·411
125·3	·131	·137	·138	450	2·786	2·766	2·798
134·3	·162	·170	·174	500	3·164	3·122	3·149
144·1	·200	·216	·218	550	3·489	3·438	3·465
153·7	·241	·265	·267	600	3·768	3·708	3·749
162·8	·286	·321	·318	650	4·013	3·947	3·999
173·3	·343	·382	·386	700	4·223	4·154	4·222
182·0	·395	·442	·444	750	4·405	4·334	4·414
191·4	·455	·513	·518	800	4·554	4·490	4·580
200·9	·520	·586	·595	850	4·694	4·627	4·717
211·8	·602	·672	·685	900	4·811	4·746	4·833
231·1	·760	·834	·858	950	4·910	4·849	4·923
241·1	·845	·925	·918	1,000	5·002	4·946	4·992
252·4	·947	1·026	1·032	1,050	5·076	5·030	5·034
264·3	1·057	1·129	1·136	1,100	5·148	5·099	5·060

On comparing the values calculated from Debye's formula ($\nu_m = 1332$ cm.$^{-1}$) with those obtained from the spectroscopic data, we notice that till about 100° K. the two results agree closely. Above 100° K. and up to about 400° K. the values given by Debye's formula progressively fall off, the difference between the two calculated values ranging up to as much as 13%.

From 400° K. to 1100° K. the values according to Debye are consistently higher than those calculated from the spectroscopic data. The difference, however, never exceeds 2%.

When we compare the calculated values with the observed ones, we find excellent agreement between the spectroscopic values and the experimental data throughout the temperature range covered by Pitzer and indeed precisely in the region where the values given by the Debye formula show the largest deviations from the observed ones. This situation is exhibited graphically in Fig. 1; the crosses indicating the observed values, while the full line and the

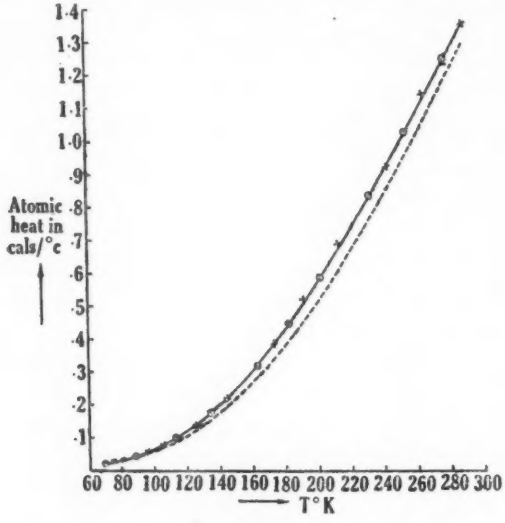

FIG. 1

dotted line represent the values calculated from the spectroscopic frequencies and Debye's formula respectively.

The agreement between the spectroscopically calculated atomic heat and the data of Magnus and Hodler is quite good except in the lowest part of the temperature range covered by the work of these authors where the latter are a few per cent. higher. It may be remarked, however, that the values of Magnus and Hodler run a little higher than those of Pitzer in this range. It seems possible therefore that Magnus and Hodler's data are systematically a little too high. In any case, little importance can be attached to the small deviations (not larger than about 2%) between the experimental data and the spectroscopically calculated values that appear in the range between 400° K. and 1000° K.; for, on the one hand, Magnus and Hodler have assumed that

the factor A in the semi-empirical formula,

$$C_p - C_v = A\, C^2_p\, T,$$

is constant over the whole range covered by them, and on the other hand, we have not taken into account the lowering of the spectroscopic frequencies with the rise of temperature.

In conclusion, the author wishes to record his deep sense of gratitude to Professor Sir C. V. Raman for his helpful interest and suggestions throughout the preparation of this paper.

Summary

It is known that the atomic heat data of diamond are not satisfactorily represented over the entire range (covered by the data) by a single Debye term assuming some one value of the limiting frequency of the elastic spectrum. In the present paper it is shown that the formula fails because Debye's hypothesis does not correctly represent the vibration spectrum of this crystal. The lattice spectrum of diamond is in fact shown by the Raman effect studies of Bhagavantam and the luminescence and ultra-violet absorption spectra studied by Nayar to consist of monochromatic frequencies down to much below the limiting frequency of Debye. The atomic heat data obtained by Pitzer agree perfectly with a formula containing Einstein terms corresponding to the spectroscopically observed frequencies of the lattice, namely 1332 cm.$^{-1}$ and 780 cm.$^{-1}$ and superlattice frequencies of 532 cm.$^{-1}$ and 218 cm.$^{-1}$, their relative weights being 4, 3, 7/8 and 1/8 respectively as indicated by dynamical considerations.

REFERENCES

Bhagavantam	..	*Ind. Jour. Phys.*, 1930, **5**, 169, 573.
Debye	..	*Ann. der Phys.*, 1912, **39**, 789.
Dewar	..	*Proc. Roy. Soc.*, 1905, A, **76**, 329.
Einstein	..	*Ann. der. Phys*, 1907, **22**, 180.
Magnus and Hodler	..	*Ibid.*, 1926, **80**, 808.
Nagendra Nath	..	*Proc. Ind. Acad. Sci.*, 1934, **1**, 333.
Nayar	..	*Ibid.*, 1941, **13**, 284, 483, 534; 1941, **14**, 1.
Nernst	..	*Ann. der Phys.*, 1911, **36**, 395.
—— and Lindemann	..	*Ber. Berl. Akad.*, 1911, **1**, 494; *Zeit. f. Elek-chem.*, 1911, **17**, 817.
Pitzer	..	*J. Chem. Phys.*, 1938, 6, 68.
Placzek	..	*Handbuch der Radiologie*, 1934, **6**, 297 (2nd Edition, Part 2).
Ramaswamy	..	*Ind. J. Phys.*, 1930, **5 (1)**, 97; *Nature*, 1930, **125 (2)**, 704.
Reinkober	..	*Ann. der Physik*, 1911, **34**, 343.
Robertson and Fox	..	*Nature*, 1930, **125 (2)**, 704.
——, —— and Martin	..	*Phil. Trans. Roy. Soc.*, 1934, A, **232**, 463; *Proc. Roy. Soc.*, 1936, A, **157**, 579.
Venkatarayudu	..	*Proc. Ind. Acad. Sci.*, 1939, **8**, 349.
Weber	..	*Phil. Mag.*, 1875, **49**, 161.

THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: MAGNESIUM, ZINC AND CADMIUM

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1. Introduction

In the form originally given, Debye's theory disregarded the crystalline nature of substances altogether. Its complete failure to account for the specific heats of metals crystallising in the hexagonal system was later ascribed to the anisotropy of single crystals of these substances which would, in general, give a different wave velocity and hence a different limiting frequency for each direction. On a close examination, however, it is found that the specific heat curves of such solids cannot always be represented in such a manner. If we replace the sum of a number of Debye functions by only one such function, but with a variable parameter, the latter would lie closer to the one appearing in the Debye function with lowest parameter at low temperatures, and increase as we go higher up. This is shown in the graph (Fig. 1) which represents the sum of two Debye functions ($\theta = 400$ and $\theta = 200$) with only one parameter. The θ Debye curves of zinc and cadmium do show such a behaviour through a large range of temperature in which it increases with temperature. In magnesium, however, the case is just the reverse. It is well known that the Einstein function increases more rapidly as the temperature is raised than the Debye function. The above behaviour of magnesium, therefore, definitely points to the presence of a low-frequency monochromatic oscillation which will increase the specific heat at higher temperatures to a larger extent than would be done by one single Debye function. [*Cf.* Fig. 1 where θ_D curve represents the sum of an Einstein function ($\theta = 200$), and a Debye function ($\theta = 250$).]

In an earlier paper of this series the author has shown that the specific heat formula for all metals in the cubic system must necessarily include one or more Einstein functions corresponding to the symmetry of their crystal structure. In the present paper this work is extended to three metals crystallising in the hexagonal system.

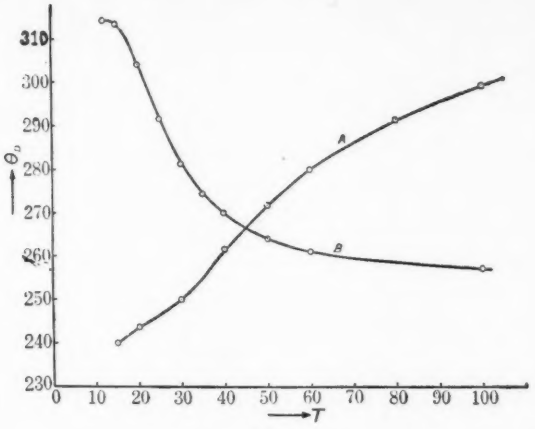

FIG. 1

Curve A–θ_D to represent $\frac{3}{2}R\left[D\left(\frac{400}{T}\right)+D\left(\frac{200}{T}\right)\right]$

Curve B–θ_D to represent $\frac{3}{2}R\left[D\left(\frac{250}{T}\right)+E\left(\frac{200}{T}\right)\right]$

2. *Relation to Crystal Structure*

All the three metals now under consideration have a hexagonal structure in which there are two atoms per unit cell. The positions of the atoms when referred to hexagonal axes are 0, 0, 0 and $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$. There are six degrees of freedom for the basis group, three of which represent the translations of the whole cell in different directions. The remaining three naturally go over to the lattice frequencies, which may be pictured as arising from the mutual oscillations of the two atoms. In the single crystals of these metals, most of the properties such as thermal expansion and elastic constants are strongly anisotropic, the values along the hexagonal axis being completely different from those in directions parallel to the basal plane. In the basal plane itself, no particular axis is favoured. In such a case we are obviously not justified in taking one representative Einstein frequency for all the three degrees of freedom. We have therefore taken two Einstein frequencies, the lower of which corresponding to movements parallel to the hexagonal axis is assigned one degree of freedom, while the higher one is assigned two degrees of freedom. As already explained in the previous papar on metals crystallising in the cubic system, we have also to include the contributions due to a series of superlattice frequencies. For simplicity we will ignore the splitting of these frequencies due to anisotropy. The formula for specific heat then becomes, only four orders of superlattice frequencies being taken,

$$C_v = 3R\left[\frac{1}{3}\left(\frac{h\nu_1}{kT}\right) + \frac{1}{6}\left(\frac{h\nu_2}{kT}\right) + \frac{7}{16}E\left(\frac{h\nu_3}{kT}\right) + \frac{7}{16\cdot 8}E\left(\frac{h\nu_4}{kT}\right) + \frac{7}{16\cdot 8\cdot 8}E\left(\frac{h\nu_5}{kT}\right) + \frac{1}{16\cdot 8\cdot 8}E\left(\frac{h\nu_6}{kT}\right)\right]$$

The total contribution of superlattice frequencies is given in the second column of the following tables.

3. *Evaluation of Specific Heats*

(*a*) *Magnesium.*—

$\nu_1 = 6\cdot 49 \times 10^{12}$, $\nu_2 = 3\cdot 55 \times 10^{12}$, $\nu_3 = 4\cdot 92 \times 10^{12}$,
$\nu_4 = 2\cdot 32 \times 10^{12}$, $\nu_5 = \nu_6 = 1\cdot 05 \times 10^{12}$.

(*b*) *Zinc.*—

$\nu_1 = 5\cdot 23 \times 10^{12}$, $\nu_2 = 1\cdot 92 \times 10^{12}$, $\nu_3 = 3\cdot 35 \times 10^{12}$,
$\nu_4 = 1\cdot 47 \times 10^{12}$, $\nu_5 = 0\cdot 88 \times 10^{12}$, $\nu_6 = 0\cdot 36 \times 10^{12}$.

(*c*) *Cadmium.*—

Since the values of C_v are not given in the paper of Lange and Simon from which the experimental data are taken, they were calculated by the usual formula

$$C_p - C_v = A\,C_p^2\,T, \text{ where } A = \frac{9\,\alpha^2\,V}{J\,k\,C_p^2}$$

(α = coefficient of linear expansion; V = atomic volume, J = mechanical equivalent of heat, k = compressibility.) The constants used were (all to 0° C.)

$k = 2\cdot 27 \times 10^{-12}$ $\qquad$ $C_p = 5\cdot 32$

$\alpha = 38 \times 10^{-6}$ $\qquad$ $V = 13\cdot 0$.

A was found to be $4\cdot 7 \times 10^{-5}$.

$\nu_1 = 3\cdot 55 \times 10^{12}$, $\nu_2 = 1\cdot 17 \times 10^{12}$, $\nu_3 = 2\cdot 34 \times 10^{12}$,
$\nu_4 = \nu_5 = \nu_6 = 0\cdot 84 \times 10^{12}$

4. *Remarks on the Frequencies Assumed*

Table IV compares the lattice frequencies with those obtained from the Lindemann melting point formula. In the case of magnesium, the frequency obtained from the Lindemann melting point formula is practically the same as has been used for specific heat evalautions, but in the other two cases it is nearly equal to the average of the two frequencies. This is presumably connected with the difference in their structure. Magnesium is a close-packed structure representing the way in which a number of spheres could be most densely packed together. The packing in zinc and cadmium on the other hand is rather loose, the axial raito c/a being much larger than is the case with magnesium. This difference is also reflected

TABLE I: *Magnesium*

Experimental Data of Clusius and Vaughen (1930)

Absolute temperature	Einstein contribution ν_3, ν_4, ν_5	Einstein contribution ν_2	Einstein contribution ν_1	Calculated C_v	Observed C_v	Difference observed −calculated	Debye function $\theta=365$	Difference observed C_v −Debye C_v
11·31	·0129	..	..	·0129	·013	+·0001	·0135	−·0005
11·41	·0135	..	..	·0135	·013	−·0005	·014	−·001
14·14	·0258	·0009	..	·027	·026	−·001	·027	−·001
16·94	·0436	·0044	..	·048	·049	+·001	·047	+·002
19·50	·0659	·0124	..	·078	·075	−·003	·071	+·004
21·7	·0857	·024	..	·110	·112	+·002	·098	+·014
27·1	·163	·074	·0029	·240	·246	+·007	·190	+·056
30·2	·220	·114	·0073	·341	·353	+·012	·261	+·092
34·2	·3111	·1727	·0189	·503	·533	+·03	·375	+·158
45·2	·6363	·3425	·0981	1·077	1·122	+·045	·803	+·419
55·1	·9616	·4753	·2273	1·664	1·720	+·056	1·292	+·428
63·7	1·2306	·5657	·3663	2·163	2·206	+·043	1·732	+·474
86·7	1·790	·7275	·751	3·269	3·223	−·046	2·818	+·405
93·2	1·909	·7585	·846	3·514	3·515	+·001	3·072	+·443
99·2	2·004	·782	·9296	3·716	3·682	−·034	3·288	+·394
106·7	2·1108	·8073	1·0243	3·942	3·836	−·106	3·54	+·296
115·4	2·210	·8315	1·1222	4·164	4·147	−·017	3·79	+·357
124·2	2·3017	·851	1·2087	4·362	4·363	+·001	4·01	+·353
136·2	2·396	·8719	1·3098	4·578	4·564	−·014	4·27	+·294
145·4	2·4486	·8855	1·3783	4·712	4·742	+·030	4·44	+·302
163·4	2·5475	·9083	1·482	4·938	4·960	+·022	4·71	+·25
272·6	2·5900	·915	1·526	5·031	5·071	+·04	4·821	+·25
182	2·6342	·9236	1·5687	5·127	5·100	−·027	4·927	+·173
191·2	2·6600	·9293	1·6023	5·192	5·118	−·074	5·001	+·117
217·2	2·7280	·9437	1·6787	5·350	5·291	−·059	5·196	+·095
228·4	2·7500	·9483	1·7053	5·404	5·339	−·065	5·26	+·079

TABLE II: *Zinc*

Experimental Data of Keesom and Ende (3·2 *to* 20)° *K. and Clusius and Harteck* (21·9 *to* 201·9)° *K.*

Absolute temperature	Einstein contribution $\nu_3, \nu_4, \nu_5, \nu_6$	Einstein contribution ν_2	Einstein contribution ν_1	Calculated C_v	Observed C_v	Difference observed −Calculated	Debye function $\theta=205$	Difference observed C_v −Debye C_v
3·2	·00082	..	..	·00082	·00093	+·00011	·00177	−·00084
3·6	·00118	..	..	·00118	·00122	+·00004	·00253	−·0013
4	·00168	..	..	·00168	·00155	−·00013	·00347	−·0019
6	·00527	..	..	·00527	·00476	−·00051	·01170	−·0069
8	·0140	·0013	..	·0153	·0152	−·0001	·0278	−·0126
10	·0302	·00849	..	·0387	·0387	±·0000	·0542	−·0155
12	·0536	·0273	..	·0809	·0792	−·0017	·0933	−·014
16	·120	·1051	..	·225	·219	−·006	·221	−·002
18	·165	·1584	·0004	·324	·327	+·003	·311	+·016
20	·2176	·2153	·0012	·434	·489	+·055	·424	+·065
21·9	·2768	·2705	·0028	·550	·537	−·014	·543	−·006
26·5	·4536	·3961	·0141	·864	·899	+·035	·895	+·004
34·3	·8165	·5633	·114	1·494	1·514	+·02	1·59	−·085
43·9	1·264	·696	·219	2·179	2·252	+·073	2·444	−·192
54·2	1·650	·7845	·4282	2·868	2·90	+·032	3·198	−·346
71·8	2·0952	·8679	·7883	3·751	3·723	−·028	4·11	−·387
85·5	2·317	·903	1·02	4·240	4·174	−·066	4·54	−·366
104·1	2·505	·931	1·255	4·691	4·611	−·08	4·947	−·336
140·9	2·707	·958	1·535	5·200	5·196	−·004	5·368	−·172
154·8	2·753	·9642	1·6023	5·320	5·299	−·021	5·466	−·167
178·2	2·804	·9703	1·6903	5·465	5·410	−·055	5·558	−·148
201·9	2·843	·975	1·744	5·562	5·517	−·045	5·664	−·147

Since there is no constant θ Debye below 12° K, its value in the column 8 has been taken from the value given by Clusius and Harteck for the T^3 region (12–20)° K. The order of error at low temperatures can be judged from the fact that at 20·09° Clusius and Harteck's value is ·421, about 16% less than that given above from Keesom and Ende.

TABLE III: *Cadmium*

Experimental Data of Lange and Simon

Absolute temperature	Einstein contribution ν_3, ν_4	Einstein contribution ν_2	Einstein contribution ν_1	Calculated C_v	Observed C_v	Difference observed −calculated	Debye function $\theta=119$	Difference observed C_v −Debye C_v
10	·117	·116	..	·233	·215	−·018	·216	+·001
20	·575	·536	·029	1·14	1·12	−·02	1·61	−·49
30	1·248	·748	·222	2·22	2·25	+·03	3·03	−·78
40	1·751	·845	·527	3·12	3·18	+·06	3·97	−·79
50	2·096	·896	·819	3·81	3·86	+·05	4·56	−·70
60	3·322	·924	1·057	4·30	4·32	+·02	4·94	−·62
70	2·476	·941	1·240	4·66	4·63	−·03	5·18	−·55
80	2·583	·953	1·378	4·91	4·84	−·07	5·35	−·51
90	2·647	·962	1·477	5·09	5·06	−·03	5·47	−·41
100	2·719	·967	1·567	5·25	5·19	−·06	5·56	−·37
110	2·763	·971	1·631	5·37	5·28	−·09	5·61	−·33
150	2·856	·982	1·788	5·63	5·50	−·13	5·77	−·27
200	2·909	·986	1·869	5·76	5·60	−·16	5·85	−·25

TABLE IV

Comparison of Frequencies

Substance	Frequency from Lindemann		Frequency used	
	$\nu \times 10^{-12}$	$\theta = \frac{h\nu}{k}$ deg. K	$\nu \times 10^{-12}$	$\theta = \frac{h\nu}{k}$ deg. K
Magnesium	6·31	302	6·49 3·55	310 170
Zinc	3·87	185	5·23 1·92	250 92
Cadmium	2·43	116	3·55 1·17	170 56

in the fact that whereas the lower frequency of magnesium is a little more than half of the higher, in the other two cases the ratio of the higher to the lower frequency is 3 : 1 nearly.

In conclusion the author wishes to express his grateful thanks to Professor Sir C. V. Raman, KT., F.R.S., N.L., for the interest he has taken in the work.

5. *Summary*

The specific heat curves of the metals having hexagonal structure cannot always be expressed in terms of a Debye function even when the anisotropy of the crystals is taken into account. It has been shown that monochromatic Einstein frequencies must be present in order to explain the peculiar shapes of these curves. At least two such frequencies must be present, the smaller of which corresponds to movements of the atoms parallel to the hexagonal axis, the higher to those in the basal plane. The specific heats of such metals can, therefore, be calculated by taking two lattice frequencies, the lower of which is given one and the higher two degrees of freedom. Einstein terms corresponding to superlattice frequencies of rapidly diminishing weight have also to be included. Such calculations have been made for magnesium, zinc and cadmium and are found to show an excellent agreement with experimental results.

REFERENCES

1. Dayal .. *Proc. Ind. Acad. Sc.* 1941, **14.**
2. Clusius and Harteck .. *Zs. f. Phys. Chemie*, 1928, **134,** 256.
3. Keesom and Ende .. *Leiden Communications*, 1932, No. 219 *b.*
4. Lange and Simon .. *Zs. f. Phys. chemie*, 1928, **134,** 376.
5. Clusius and Vaughen .. *J. Am. Chem. Soc.*, 1930, **52,** 4686.

THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: QUARTZ

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1. Introduction

Saxena (1940) carried out a detailed analysis of the Raman and infra-red spectra of quartz and identified the twenty-four fundamental frequencies of the quartz lattice, assuming that the three silicon and six oxygen atoms forming the basis group vibrate in identically the same way in all the lattice cells of the crystal. Each of the fundamental frequencies of the lattice represents an Einstein function in the expression for the specific heat of the crystal which can therefore be evaluated by summing up the functions. That Saxena's identification of the fundamental frequencies is correct is indicated by the satisfactory agreement of the specific heats thus calculated by him with those experimentally determined over a wide range of temperatures. It is to be remarked that the three degrees of freedom (out of the total of twenty-seven) remaining unrepresented by Einstein terms appear in Saxena's expression for the specific heat as a Debye term. A characteristic Debye temperature of 204° T. corresponding to a limiting frequency of 142 cm.$^{-1}$ was chosen by him as giving the best fit with the experimental data, without considering the question whether this assumption could be reconciled with the known elastic constants of quartz.

In view of the rather arbitrary choice of the Debye limiting frequency made by Saxena, the specific heat data of quartz are further examined in the present paper. The situation is best exhibited by deducting from the observed specific heats the sum-total of the contributions of the 24 Einstein terms and comparing the differences thus obtained with the Debye function assumed. The tabulations necessary for this purpose are made in Table I. Here the specific heats in calories per gram molecular weight (180·9 gm. for 3 SiO_2) are shown, the data from 25°·8 T. to 36°·1 T. being taken from the early work of Nernst, the values from 53°·4 T. to 296°·1 T. from the recent work of Anderson (1936), and the values at still higher temperatures from the observations of Moser (1936). The last column of Table I thus shows the residual specific heat due to the three unassigned degrees of freedom. It will

TABLE I

1	2	3	4	5	6
Absolute temperature T.°	Total specific heat C_p observed	$C_p - C_v$	Total specific heat C_v observed	Internal vibrations contribution $C_{v_i} = \sum_1^{24} RE\left(\frac{h\nu_i}{kT}\right)$	$C_{v_o} - C_{v_i}$
25·8	1·25		1·25	0·17	1·08
28·75	1·56		1·56	0·28	1·28
31·2	1·58		1·58	0·40	1·18
36·1	2·38		2·38	0·69	1·69
53·4	4·65		4·65	2·05	2·60
60·3	5·56		5·56	2·71	2·85
80·0	8·58		8·58	4·63	3·95
98·9	11·04		11·04	6·70	4·34
122·1	14·29		14·29	9·33	4·96
156·2	18·69		18·69	13·12	5·57
184·8	21·99		21·99	16·09	5·90
216·1	25·07		25·07	19·08	5·99
252·1	28·49	0·15	28·34	22·20	6·14
272·0	30·54	0·20	30·34	23·76	6·58
296·1	31·74	0·25	31·49	25·56	5·93
316·5	33·84	0·27	33·57	26·97	6·60
381·1	37·24	0·40	36·84	30·85	5·99
428·8	39·66	0·50	39·16	33·18	5·98
475·8	41·88	0·63	41·25	35·04	6·21
565·3	45·54	1·00	44·54	37·86	6·68
670·0	48·56	1·74	46·82	40·26	6·56
777·3	52·71	4·03	48·68	41·84	6·84
808·6	54·95	5·88	49·07	42·21	6·86

be noticed that this reaches the limiting value of 5·96 at about 200° T., remains approximately constant upto about 428° T. and then definitely rises beyond the limit at higher temperatures. The last column of Table I is carried over to the second column of Table II for comparison with the theoretical values obtained in different ways. In column three are shown the values calculated from the Debye function assumed by Saxena. It will be seen that over the range from 31° T. to 122° T. these are definitely in excess of the observed values by ten to twenty-five per cent. In the hope of finding an explanation for this discrepancy, the present author has evaluated the Debye limiting frequency from the known elastic data for quartz in different directions. The characteristic temperature calculated in this way comes out to be 271° T. corresponding to a limiting frequency of 189 cm.$^{-1}$ The values of the corresponding Debye function are tabulated in column four of Table II. It will be seen that the situation is now reversed, the calculated values being considerably smaller than the experimental values. The differences become larger as we approach the lower end of the temperature range covered by Anderson's experimental data, while the calculated values are altogether too small in

TABLE II

1	2	3	4	5
Absolute temperature T.°	Observed $C_v - C_{v_i}$	3 RD $\left(\frac{204}{T}\right)$	3 RD $\left(\frac{271}{T}\right)$	RE $\left(\frac{h\nu_1}{kT}\right)$ +2 RE $\left(\frac{h\nu_2}{kT}\right)$*
25·8	1·08	0·85	0·39	0·74
28·75	1·28	1·10	0·53	0·95
31·2	1·18	1·32	0·66	1·14
36·1	1·69	1·78	0·96	1·52
53·4	2·60	3·16	2·14	2·78
60·3	2·85	3·57	2·57	3·19
80·0	3·95	4·40	3·57	4·07
98·9	4·34	4·87	4·20	4·61
122·1	4·96	5·20	4·72	5·02
156·2	5·57	5·48	5·14	5·36
184·8	5·90	5·61	5·36	5·52
216·1	5·99	5·70	5·52	5·63
252·1	6·14	5·77	5·62	5·71
272·0	6·58	5·79	5·68	5·76
296·1	5·93	5·81	5·71	5·78
316·5	6·60	5·83	5·74	5·80
381·1	5·99	5·87	5·81	5·85
428·8	5·98	5·89	5·84	5·86
475·8	6·21	5·90	5·86	5·87
565·3	6·68	5·92	5·88	5·90
670·0	6·56	5·93	5·91	5·90
777·3	6·84	5·93	5·92	5·91
808·6	6·86	5·93	5·92	5·92

* ν_1 is a superlattice frequency 69 cm.$^{-1}$ and ν_2 is another superlattice frequency 145 cm.$^{-1}$ (in spectroscopic units).

the range covered by the data of Nernst. It is thus evident that the Debye function calculated from the elastic constants altogether fails to represent the specific heat at low temperatures.

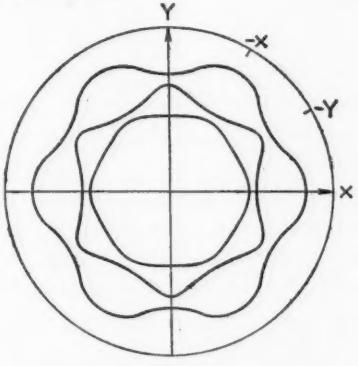

FIG. 1

Schæfer-Bergmann pattern for quartz

2. Calculation of the Debye Limiting Frequency

The total number of vibrations whose frequencies lie between ν and $\nu + d\nu$ in an anisotropic solid of volume V is according to Born

$$dz = \mathrm{V\,F}\,\nu^2\,d\nu,$$

where $\mathrm{F} = \int \left(\frac{1}{C_1^3} + \frac{1}{C_2^3} + \frac{1}{C_3^3}\right) d\Omega$, the integral being taken over the complete solid angle of 4π. Here C_1, C_2 and C_3 are the three elastic wave velocities associated with the particular direction, as given by the three real roots of the secular equation of the third degree due to Christoffel. The Debye limiting frequency is thus given by $\nu_m = \sqrt[3]{\frac{9\mathrm{N}}{\mathrm{VF}}}$. Thus, if the integrand appearing in the expression for F is averaged over the whole solid angle of 4π and if this average is $\frac{1}{C_m^3}$, then the limiting frequency can be written as

$$\nu_m = \sqrt[3]{\frac{9\mathrm{N}C_m^3}{4\pi\mathrm{V}}}.$$

The value of $\frac{1}{C_m^3}$ can be found making use of the diffraction patterns given by a quartz crystal vibrating at ultrasonic frequencies. These patterns have been obtained by Schæfer and Bergmann (1935) in the form of three curves whose radii vectores are proportional to the reciprocal of the velocities of the elastic waves along the respective directions. The scale of the curves can be evaluated with the aid of the known velocities along particular directions, such as the X, Y and Z axes. This can be done by solving the Christoffel equation and using the known values of the six elastic moduli of quartz. The latter have been determined by Voigt by numerous experiments to be $C_{11} = 854{\cdot}6$, $C_{33} = 1056{\cdot}2$, $C_{44} = 571{\cdot}2$, $C_{12} = 72{\cdot}5$, $C_{13} = 143{\cdot}5$, $C_{14} = 168{\cdot}2$, expressed in 10^9 dynes per sq. cm. It may be remarked here that Bechmann (1934) has also found the velocities of the elastic waves in quartz along certain directions, by measuring the characteristic frequencies of piezoelectrically excited plates of the crystal.

Figs. 1 to 5 represent the Schæfer–Bergmann patterns given by quartz for five different orientations of the crystal. These figures have been drawn making use of the drawings and photographs reproduced in their paper for three cases out of the five. Various alterations have however had to be made in the diagrams given by Schæfer and Bergmann which did not correctly represent the situation as found from the Christoffel equation and Voigt's elastic constants. Fig. 1 represents the pattern for a plate cut normal to the triad axis, while Figs. 2, 3, 4 and 5 refer to a plate parallel to the triad axis, but inclined to the XZ planes at angles of 0°, 10°, 20° and 30° respectively.

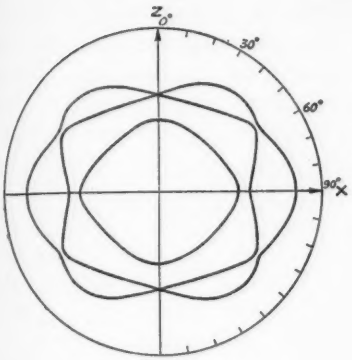

FIG. 2

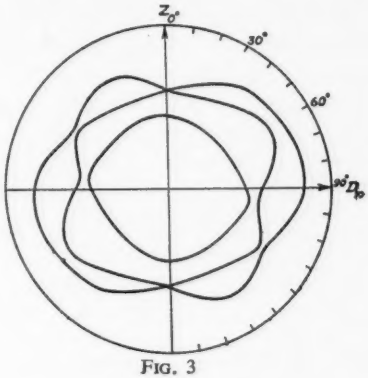

FIG. 3

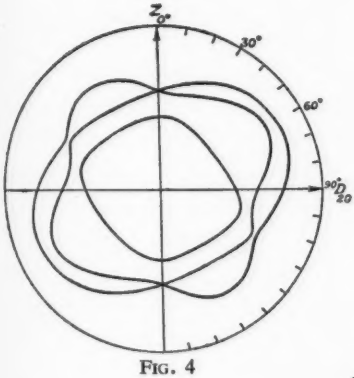

FIG. 4

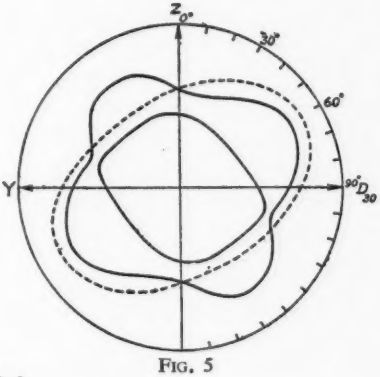

FIG. 5

FIGS. 2–5

Schæfer-Bergmann patterns of quartz

In view of the hexagonal symmetry of the pattern shown in Fig. 1, Figs. 2 to 5 were drawn to enable the entire three-sheeted surface to be visualised. The sum of the cubes of the three radii vectors of this surface averaged over planes at intervals of 10°, namely 0°, 10°, 20°, 30°, 40° and 50° gave the complete average over the whole solid angle. The general average value of $\frac{1}{C_m^3}$ in each of these planes was found to be $10^{-18} \times 34{\cdot}2$, $34{\cdot}8$, $34{\cdot}3$, $35{\cdot}4$, $34{\cdot}3$ and $34{\cdot}8$, respectively. The general average was thus $34{\cdot}6 \times 10^{-18}$. Using this value, the Debye limiting frequency comes out as 189 cm.$^{-1}$, corresponding to a temperature of 271° T.

3. *Superlattice Frequencies of Quartz*

The failure of the Debye theory is evident on comparison of the figures in the second and fourth columns in Table II. Since the elastic constants of

quartz are precisely known, it can scarcely be suggested that this failure can be regarded otherwise than as definitely indicating the unjustifiable character of the assumptions on which the Debye theory is based. Mr. Saxena's investigation shows that twenty-four out of the twenty-seven degrees of freedom of vibration of the lattice cell are represented by discrete or monochromatic frequencies of vibration. Since the bonds which link the lattice cell together are of the same nature as those that join the atoms within the cell, it must be presumed that even the three remaining degrees of freedom of translation of the lattice cell must also be represented by discrete superlattice frequencies, as explained by Sir C. V. Raman in a paper appearing earlier in this issue. A re-examination of several well-exposed Raman spectra of quartz obtained by Mr. T. M. K. Nedungadi and Mr. B. D. Saxena at this Institute showed some faint lines with relatively small frequency shifts, which had been previously overlooked. The most prominent of those lines has a frequency shift of 145 cm.$^{-1}$ This line is easily recognizable on all sufficiently well-exposed spectra. Another line with a frequency shift of 69 cm.$^{-1}$ which is less intense is very clearly recorded in Mr. Nedungadi's best plates and also in some of Mr. Saxena's photographs. As they worked with different instruments, there can be no doubt as to the reality of this line. A third line at 95 cm.$^{-1}$ is also seen in two of Mr. Nedungadi's best pictures and must also be presumed to be real.

As the theory of the superlattice vibrations of quartz has not been worked out in detail, the statistical weight to be attached to these three frequencies in the expression for the specific heat is uncertain. We must evidently expect a series of superlattice frequencies of different orders and of rapidly diminishing statistical weight. A consideration of the higher orders would be necessary for explaining the course of the specific heat curve at the lowest temperatures. As, however, the available data go down only to 25° T., it should be sufficient for our present purpose to consider only the superlattice frequencies of the first order. The two most intense of the recorded lines, namely 145 and 69 cm.$^{-1}$ may be assumed to belong to this order. The feebler line at 95 cm.$^{-1}$ is a superlattice frequency of either the first or the second order. We shall here assume that it belongs to the second order. Hence, to a sufficient approximation, we need consider only the 145 and 69 lines, and as the former is the more intense, two degrees of freedom may be assigned to it, and the remaining third degree of freedom to the 69 line. The sum of the corresponding Einstein terms in the expression for the specific heat at various temperatures is shown in the fifth column of Table II. It will be seen that the figures are in good agreement with the unexplained residue of the specific heat shown in the second column of the same table at all

temperatures from 31° to 428° T. At the two lowest temperatures 25°·8 and 28°·75, the agreement is not so good, but the experimental data for these two temperatures are evidently unsatisfactory. At high temperatures, the specific heat distinctly tends to be anomalous as in the case of many substances. The explanation of the small discrepancy at high temperatures lies outside the scope of the present paper.

In conclusion, the author desires to record his grateful thanks to Professor Sir C. V. Raman for the kind and valuable interest which he evinced towards this work.

4. *Summary*

From the diffraction patterns obtained by Schæfer and Bergmann with quartz plates vibrating at ultrasonic frequencies, the three sound velocities in various directions in the crystal were evaluated. Thence, equating the total number of possible elastic vibrations to thrice the number of lattice cells in the crystal, the Debye limiting frequency was ascertained as 189 cm.$^{-1}$ A Debye function for this limiting frequency failed however to agree with the specific heats of quartz after allowance had been made for the contributions of the Einstein terms representing the discrete monochromatic frequencies of vibration of the lattice cell identified by Saxena (1940). The calculated values were much lower than the residual values of the specific heat. The failure of the Debye theory is thus unmistakably clear. The observed specific heats over the region of temperatures covered by Anderson's recent work (1936) are very satisfactorily explained by including further Einstein terms corresponding to the superlattice frequencies 145 cm.$^{-1}$ and 69 cm.$^{-1}$ appearing as feeble lines in the Raman spectra of quartz.

REFERENCES

1. Saxena, B. D. .. *Proc. Ind. Acad. Sci.*, 1940, **12**, 93.
2. Sosman .. *The Properties of Silica*, A. C. S. Monograph No. 37, 1927.
3. Nernst .. *Ann. d. Phys.*, 1911, **36**, 421.
4. Anderson, C. T. .. *Jour. Amer. Chem. Soc.*, 1936, **38**, 568.
5. Moser, H. .. *Phys. Zeit.*, 1936, **37**, 737.
6. Nedungadi, T. M. K. .. *Proc. Ind. Acad. Sci.*, 1940, **11**, 86.
7. Christoffel, E. B. .. See Love, *A Treatise on the Mathematical Theory of Elasticity*, 4th Edition, p. 298.
8. Voigt, W. .. *Ann. Physik u. Chem.*, 1887, **31**, 474, 701; *Lehrbuch der Kristallphysik*, Leipzig, 1910.
9. Born, M. .. *Handbuch der Physik*, Bd. **24/2**, 651; *Encyklopädie d. Mathematischen Wissenchaften*, Bd. **5**, 3, 591.
10. Be:kmann, R. .. *Zs. f. Phys.*, 1934, **91**, 670; *Hochfrequenztechnik und Elektroakustik*, 1934, **44**, 145; *Zs. techn. Phys.*, 1935, **16**, 525.
11. Schæfer and Bergmann .. *Sitz.-Ber. Berilner. Akad.*, 1935, 222.

THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: ALKALI HALIDES

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1. Introduction

In a recent paper published in these *Proceedings*, the author (1941) has applied the theory of groups to the analysis of the lattice spectrum of rock-salt. The unit cube was assumed to contain four sodium and four chlorine atoms, each group possessing tetrahedral symmetry. The character table for the crystal showed that the twenty-four degrees of freedom of the atoms in the unit cell are distributed among eight modes of triply degenerate vibrations. One of them corresponds to the translations of the cell as a whole. All of them being antisymmetric to the centre of symmetry, are forbidden in the Raman effect. Two of them appear under the symmetry class which is active in the infra-red, while the remaining five are inactive. In the present paper the author proposes to discuss these results in relation to the spectroscopic and specific heat data available for sodium and potassium chloride crystals.

2. Identification of the Lattice Frequencies of Rock-salt

The infra-red spectra.—Barnes and Czerny (1931) and Barnes (1932) have carried out detailed investigations of the infra-red absorption spectra of thin plates of several halides and shown that in every case there are at least two, if not three, absorption maxima. One of them is very pronounced and has been identified by them as the principal vibration frequency of the crystal. The others are relatively weak and in cases in which three are observed, one of them almost coincides with the rest-strahlen frequency reported by Schæfer and Matossi (1930). For rock-salt, Barnes and Czerny have given two absorption frequencies at $61{\cdot}6 \pm {\cdot}3\,\mu$ (strong) and $40{\cdot}5\,\mu$ (weak). These frequencies have to be identified with the two triply degenerate infra-red active vibrations expected from the group-theoretical analysis of the spectrum.

The Raman Spectra.—The Raman spectra of alkali halides do not ordinarily yield any line as was pointed out by Schæfer (1929) and Krishnamurti (1930). Fermi and Rasetti (1931) have subsequently published a remarkable

photograph together with a microphotometric record, of the Raman spectrum of a single crystal of rock-salt taken with 2537 Å radiations of the mercury arc. They have firstly made the observation that the spectrum of rock-salt is very weak, an exposure time of eight hours being required with particularly intense irradiation whereas the strongest Raman line of calcite was recorded in one minute. This extreme feebleness of the spectrum as well as the inability of Schæfer and Krishnamurti to observe the same with 4046 A. U. radiations is in agreement with the conclusion arrived at theoretically by the present author. Secondly, these authors have indicated that the spectrum, in the main, consists of bands, one part lying in the close proximity of the exciting line between 0 and 50 cm.$^{-1}$ and the other part lying in the region 160 to 365 cm.$^{-1}$ The region between 50 and 160 cm.$^{-1}$ shows further, a weak continuum. From their reproduced spectrum, several measurable maxima may be easily identified. While many of them are broad, a few are comparatively sharp. The author has measured this spectrum and obtained the following frequency shifts for the middle points of the maxima.

TABLE I

The Raman Frequencies of Rock-salt

No.	Centre of maxima in cm.$^{-1}$	Fundamental Frequency in cm.$^{-1}$	Intensity (Estimate)	Remarks	Assignments
1	40	20	Medium	Broad with Continuum up to 2537 A.U.	Lattice Spectrum—4th order
2	85	42	Very weak	Very broad	Lattice Spectrum—3rd order
3	162	81	Weak	do.	Lattice Spectrum—2nd order
4	228	114	Very strong	Fairly sharp	Lattice Spectrum—1st order
5	273	136	Medium	do.	
6	299	150	Strong	Broad	
7	345	173	do.	do.	
8	365	183	do.	do.	

It has been pointed out by Bhagavantam and Venkatarayudu (1939) that the first overtone of every normal mode is active in the Raman effect of especially the crystals, irrespective of whether the fundamental is permitted or forbidden. This would especially be the case for the five inactive frequencies coming under class F_{2u}. in the character table for rock-salt. For, the vibrations of the class F_{2g} are Raman active and those of class F_{2u} are similar to the latter except for the fact that they are antisymmetric to the centre of inversion, while those of F_{2g} are symmetric. The sum of the squares of the

characters of these two classes is therefore identical and accordingly, the overtones of the two classes of vibrations are equally probable. As indicated in Table I, the five frequencies, *viz.*, 228, 273, 299, 345 and 365 may be assigned to the first overtones of the vibrations of class F_{2u}. Besides the above, three bands appear with peak frequencies of 40, 85 and 162 cm.$^{-1}$ which are broader than the former. These are explained in what follows.

3. Superlattice Frequencies for Rock-salt

In a paper appearing in the present issue of these *Proceedings*, Sir C. V. Raman has indicated that in addition to the lattice vibrations of the smallest unit cell, the crystal possesses superlattice oscillations of several orders, which in favourable cases could be recorded in the Raman spectra of crystals. As the group theoretical method is equally applicable to assemblages of particles as to atoms and molecules symmetrically distributed in space, we shall analyse the superlattice vibrations by considerations similar to those applied to the unit cell itself. It will be remembered that out of the twenty-four degrees of freedom for the sodium and chlorine atoms in the unit cell, three contribute to the translations of the cell as a whole. When we consider similar motions of equivalent atoms in two neighbouring cells, there are two alternatives, *viz.*, that they may move in the same direction (*i.e.*, in phase) or in opposite directions (*i.e.*, opposite in phase). The symmetry of the crystal suggests that eight neighbouring unit cells should be treated at one time, which together have all the elements of symmetry possessed by the unit cell itself. The larger cell thus chosen (or the superlattice cell) is eight-fold in size and contents of the unit cell, and forms a face-centred cubic lattice. The problem of analysing the twenty-four degrees of freedom of translation of this larger unit thus becomes identical with the case of rock-salt which we have already considered. In general, it will be seen that there will be eight triply degenerate vibrations of which one alone is to be attributed to the translations of the unit as a whole. The remaining seven frequencies may be said to form the lattice spectrum of the second order. Taking thirty-two atoms (of Na and Cl) in this greater cell, the group theoretical analysis may be carried out rigorously. Simple considerations, however, lead to the ultimate result that each of the seven normal modes of the primary cell, while retaining their nature and frequency nearly the same, become each eight-fold, with the phase of vibration in different cells being the same or opposite as the case may be. In addition, we will get seven discrete frequencies characteristic of the superlattice of the first order. We can now repeat the process to superlattices of higher orders, each successive step yielding seven triply degenerate discrete frequencies together with three degrees of translation as a whole.

The effect of the superlattice vibrations on the normal modes of the smaller unit cell is to multiply each of the latter several-fold. Each line in a crystal thus theoretically represents a group of nearly identical frequencies and should accordingly appear broadened. This is in accordance with the experimental fact observed in several cases that the lattice Raman lines are generally broader than the internal vibrations of molecules or radicals (Venkateswaran, 1938); the latter remain comparatively unaffected by the surroundings due to the much greater strength and stability of the chemical bond involved.

It is common knowledge that the possible frequencies of an atomic group are the closer together, the greater the atomic masses and the smaller the forces between them. We should accordingly expect each group of superlattice vibrations to consist of a fairly narrow band of frequencies. Three Raman bands with their centres at 162, 85 and 40 cm.$^{-1}$ appearing in the spectrum of rock-salt (Table I) may therefore be taken as representative of the lattice spectra of the second, third and fourth orders. As in the case of the lattice vibrations of the first order and for the same reason, these frequencies should be taken as the octaves; the fundamentals being respectively 81, 42 and 20 cm.$^{-1}$

4. The Specific Heat of Rock-salt

It is obvious from the foregoing discussion that in calculating the thermal energy of the crystal, Einstein functions corresponding to the seven triply degenerate frequencies of each order of the lattice spectra should be taken into account, as these spectral lines are essentially discrete in character. As there are four NaCl groups in the unit cell, the contribution to the molar specific heat arising from the lattice vibrations of the first order is

$$\tfrac{1}{4}\Sigma_1^7\, 3\ \mathrm{R}\ \mathrm{E}(\theta_1)$$

where the $\theta_1 s$ are given by the frequencies and the temperature of observation. The second order lattice spectrum will yield

$$\frac{1}{4\times 8}\Sigma_1^7\, 3\ \mathrm{R}\ \mathrm{E}(\theta_2),$$

the third,

$$\frac{1}{4\times 8\times 8}\Sigma_1^7\, 3\ \mathrm{R}\ \mathrm{E}(\theta_3),$$

and so forth. Hence,

$$C_v\,(\text{molar}) = \frac{1}{4}\Sigma_1^7\, 3\ \mathrm{R}\ \mathrm{E}\ (\theta_1) + \frac{1}{4\times 8}\Sigma_1^7\, 3\ \mathrm{R}\ \mathrm{E}(\theta_2) + \frac{1}{4\times 8\times 8}\Sigma_1^7\, 3\ \mathrm{R}\ \mathrm{E}(\theta_3) + \text{etc.}$$

TABLE II

Table of Specific Heats of Rock-salt

Temp. in Degrees Absolute	θ_1 Values							$\frac{1}{4}\Sigma\theta_1$	θ_2 118	θ_3 54	θ_4 28	θ_5 18	Total C_v (molar) Calculated	C_v* Experimental
	229	354	164	196	214	247	262							
10	..	..	..	..	..	..	..	..	·0014	·0216	·0110	·0020	·036	·04
20	·008	..	·112	·032	·0151	·004	·0012	·0431	·1248	·0917	·0173	·0024	·28	·32
25	·128	..	·369	·149	·085	·028	·018	·1943	·2786	·1119	·0184	·0024	·605	·58
30	·166	·0062	·771	·374	·241	·107	·074	·434	·4100	·1251	·0189	·0025	·99	·96
40	·637	·0677	1·714	1·081	·813	·474	·369	1·289	·6606	·1403	·0195	·0025	2·10	2·04
50	1·300	·257	2·610	1·900	1·544	1·054	·856	2·383	·8356	·1481	·0198	·0025	3·40	3·53
60	2·011	·571	3·326	2·630	2·260	1·697	1·485	3·50	·9819	·1523	·0200	·0025	4·70	5·2
70	2·609	·986	3·850	3·218	2·89	2·262	2·077	4·48	1·031	·155	·0201	·0025	5·70	6·3
80	3·126	1·431	4·258	3·709	3·380	2·840	2·618	5·345	1·109	·1568	·0202	·0025	6·7	7·0
100	3·902	2·30	4·782	4·366	4·121	3·673	3·469	6·65	1·160	·1590	·0202	·0025	7·93	8·28
120	4·434	3·019	5·116	4·794	4·591	4·230	4·066	7·588	1·224	·1601	·0202	·0025	8·948	9·08
140	4·782	3·587	5·316	5·071	4·924	4·591	4·479	8·191	1·228	·1608	·0203	·0025	9·6	9·64
160	5·035	4·03	5·467	5·26	5·139	4·899	4·788	8·66	1·254	·1614	·0203	·0025	10·09	10·05
180	5·208	4·40	5·560	5·410	5·290	5·043	5·012	8·98	1·257	·1616	·0203	·0025	10·42	10·38
200	5·340	4·61	5·632	5·500	5·426	5·241	5·173	9·335	1·266	·1618	·0203	·0026	10·78	10·67
235	5·504	4·954	5·718	5·622	5·67	5·442	5·400	9·58	1·276	·1620	·0204	·0026	11·04	11·10
300	5·815	5·30	5·885	5·856	5·833	5·793	5·774	10·17	1·286	·1624	·0204	·0026	11·54	11·60
Maximum	6	6	6	6	6	6	6	10·5	1·3125	·1643	·0205	·0027	12	..

* These experimental values are those obtained by Nernst and given in *Landolt-Börnstein Tabellen*. They show small variations from those given in the *Handbüch der Experimental Physik* and in the *International Critical Tables* and have therefore to be considered as not of a high order of accuracy.

From the infra-red and Raman spectra we have identified the following seven frequencies for the first order lattice spectrum of rock-salt: 161, 247, 114, 136, 150, 173 and 183 cm.$^{-1}$ These give the $\theta_1 s$. As there is at present no spectroscopic method of ascertaining all the seven frequencies belonging to higher orders, it will be assumed, as a first approximation, that they may each be represented by a single frequency for the purpose of the calculation of specific heat. The three Raman frequencies given in Table I, *viz.*, 81, 38 (instead of 42) and 20 cm.$^{-1}$ are chosen for θ_2, θ_3 and θ_4. In addition, 13 cm.$^{-1}$ is chosen as the representative lattice frequency of the fifth order from a perusal of the specific heat data at 20° absolute.

5. *Table of Specific Heats for Rock-salt*

Assuming the above values of frequencies, Table II exhibiting the specific heats is prepared for rock-salt for the temperature range of 10° – 300° T. The experimental values of specific heat are taken from Landolt and Börnstein Tabellen, and corrected for the work done for the expansion of the crystal by making use of the relation $C_p - C_v = 2{\cdot}7 \times C_p^2 \times T \times 10^{-5}$ per gram atom, given in the *Handbuch der Experimental Physik*.

6. *The Specific Heat of Sylvine*

Exhaustive data for the specific heat of potassium chloride are given by Keesom and Clark (1935) from 3° to 17° T. and by Southard and Nelson (1933) from 17° to 285° T. and are therefore, particularly suitable for the verification of the above expression for the specific heat of crystals. The two infra-red active frequencies recorded for this crystal by Barnes and Czerny are 141 and 212 cm.$^{-1}$ corresponding to the absorption maxima at 70·7 μ (strong) and, 47 μ (weak). Unfortunately the Raman spectrum of sylvine has not been recorded as in the case of rock-salt. However, the remaining frequencies could be deduced from those of the latter on the assumption that $\nu \approx 2\pi\sqrt{\frac{f}{\mu}}$. Since the force between K^+ and Cl^- is Coulombian, it may be varies as the square of the distance between the atoms, *i.e.*, half the edge of the unit cube. This gives the relation

$$\frac{\nu_{KCl}}{\nu_{NaCl}} = \sqrt{\frac{(2{\cdot}814)^2 \times 13{\cdot}95}{(3{\cdot}14)^2 \times 18{\cdot}61}} = 0{\cdot}78$$

The corresponding ratio of the infra-red active frequencies being 0·86, it may without serious error be assumed that the average ratio of 0·78 may be used for the purpose of calculation. The frequencies of the lattice spectrum of the first order for KCl thus obtained are $\nu_1 = 141$, $\nu_2 = 212$, $\nu_3 = 89$, $\nu_4 = 107$, $\nu_5 = 116$, $\nu_6 = 135$ and $\nu_7 = 143$ cm.$^{-1}$ The representative frequencies chosen

TABLE

The Specific

Temp.* in Degrees Absolute	θ_1 VALUES							$\frac{1}{4}\Sigma\theta_1$
	202	304	128	153	167	194	205	
2·99	..	..	..	..	..	..	..	..
3·52	..	..	..	..	..	..	..	..
4·01	..	..	..	..	..	..	..	..
4·6	..	..	..	..	..	..	..	..
5·14	..	..	..	..	..	..	..	..
5·72	..	..	..	..	..	..	..	..
6·52	..	..	..	..	..	..	..	..
7·65	..	..	..	..	..	..	..	..
8	..	..	..	..	..	..	..	..
9·23	..	..	..	..	..	..	..	..
10·06	..	..	·0027	..	..	..	..	·0007

* These temperatures were chosen out of the numerous

TABLE

Temp. T° C.	202	304	128	153	167	194	205
13·55	..	..	·0435	·0093	·0041	·0035	..
14·73	·0013	..	·0776	·0196	·0093	·0079	·0011
16·67	·0048	..	·166	·051	·027	·0237	·0043
21·21	·0392	..	·521	·221	·138	·053	·034
32·41	·456	·044	1·88	1·277	·932	·546	·430
39·86	·974	·168	2·701	1·97	1·641	1·118	·932
49·27	1·715	·466	3·502	2·815	2·482	1·877	1·660
59·61	2·564	·956	4·120	3·531	3·218	2·616	2·414
69·92	3·086	1·493	4·552	3·916	3·772	3·308	2·946
79·11	3·557	1·970	4·819	4·396	4·176	3·626	3·517
89·28	3·957	2·458	5·041	4·686	4·490	4·096	3·902
101·31	4·312	2·954	5·222	4·942	4·770	4·433	4·285
121·41	4·751	3·626	5·442	5·237	5·104	4·845	4·719
141·17	5·036	4·108	5·568	5·405	5·303	5·104	5·011
163·45	5·244	4·536	5·662	5·534	5·467	5·303	5·232
179·76	5·370	4·718	5·717	5·608	5·533	5·425	5·353
201·32	5·483	4·942	5·750	5·676	5·624	5·602	5·476
240·7	5·645	5·219	5·816	5·756	5·724	5·648	5·608
284·7	5·711	5·279	5·826	5·813	5·788	5·732	5·704
Maximum	6	6	6	6	6	6	6

III

Heats of Sylvine

θ_2 80	θ_3 42	θ_4 22	θ_5 14	$\theta_6+\theta_7$, etc.	Total C_v (molar) Calculated	C_v Experimental
..	..	·00072	·00052	·00032	·0016	·00206
..	·00024	·00156	·00078	·00032	·0029	·00338
..	·00074	·00256	·00101	·00032	·0046	·00470
..	·00206	·00397	·00124	·00032	·0076	·00724
..	·00315	·00534	·00142	·00032	·0102	·0101
..	·0057	·0067	·0016	·00032	·0143	·0145
·0009	·0108	·0085	·0017	·00032	·0219	·0191
·0041	·0204	·0106	·0019	·0003	·0373	·0368
·0058	·0238	·0111	·0020	·0003	·0430	·0460
·0169	·0391	·0129	·0021	·0003	·0710	·0620
·0291	·0449	·0138	·0022	·0003	·0907	·0840

data available, at regular intervals.

III (*Contd.*)

$\frac{1}{4}\Sigma\theta_1$	θ_2 80	θ_3 42	θ_4 22	θ_5 14	C_v Calculated	C_v Observed
·0151	·1248	·0773	·0164	·0023	·236	·238
·0292	·1697	·0862	·0169	·0024	·304	·310
·0692	·2511	·0984	·0176	·0024	·439	·438
·252	·4477	·1186	·0186	·0025	·839	·842
1·391	·8024	·1417	·0196	·0025	2·357	2·358
2·376	·9410	·1488	·0199	·0025	3·488	3·52
3·629	1·051	·1533	·0200	·0025	4·856	4·91
4·855	1·122	·1563	·0201	·0025	6·156	6·30
5·768	1·168	·1581	·0202	·0025	7·117	7·33
6·515	1·198	·1591	·0203	·0026	7·895	8·12
7·205	1·222	·1599	·0203	·0026	8·610	8·77
7·729	1·237	·161	·0204	·0026	9·150	9·35
8·431	1·256	·161	·0204	·0026	9·871	10·04
8·884	1·268	·161	·0205	·0026	10·336	10·60
9·245	1·275	·162	·0205	·0026	10·705	10·96
9·431	1·280	·162	·0205	·0026	10·90	11·13
9·638	1·283	·162	·0205	·0026	11·106	11·32
9·854	1·290	·162	·0205	·0026	11·329	11·58
9·963	1·295	·162	·0205	·0026	11·443	11·72
10·5	1·3125	·1643	·0205	·0027	12	..

for the second to the fifth orders are respectively 56, 29, 15, and 10 cm.$^{-1}$ It will be noticed that these latter frequencies for the two salts are nearly in the ratio 1 : 0·78. The lattice spectra of orders higher than five are assumed to make their maximum contribution of ·00032 calories per gm. mol. per degree. $C_p - C_v$ for sylvine is given by 2 $C_p^2 \times 10^{-5}$ calories per gram atom.

7. *Significance of the Results*

The failure of Debye's theory of specific heat in these two cases is well known. Following Born's theory, Blackman (1935), Kellermann (1941) and others have sought to explain this latter as due to a variation of the characteristic temperature of the cyrstals. Keesom and Clark (1935) have pointed out that this variation of characteristic temperature is anomalous in the case of sylvine at low temperatures. Important deviations from the Debye formulæ in the case of rock-salt have been reported by Clausius, Goldman and Perlick (1934). It will be seen from Tables II and III that the values of specific heats calculated on the basis of the spectroscopic facts agree reasonably well with the observed data for both the crystals throughout the whole range of temperature, which in the case of sylvine nearly approaches the absolute zero. The investigation thus clearly demonstrates that the present approach to the theory of specific heat should replace the earlier ones due to Debye, Born and others.

An examination of the contributions to the thermal energy of each of the orders of the lattice spectra reveals interesting features, giving an insight into the distribution of the thermal energy at various temperatures. The contributions by orders higher than five become significant only at extremely low temperatures (less than 5° T.), the contribution of the first two orders of spectra then vanishing. As the temperature is raised to 50° for rock-salt and 40° for sylvine, the fifth and the fourth orders attain their maximum value of ·0026 and 0·205 respectively. The contributions of the second and the third orders increase less quickly, becoming the maximum at about 100° T. At room temperature, practically 6/7 of the total energy (*i.e.*, 10·5 out of 12) is due to the lattice vibrations of the first order. The whole of the thermal energy of the crystal can be represented by considering a superlattice cell of edge length 50×10^{-8} cm.

In conclusion the author wishes to thank Sir C. V. Raman for his keen and abiding interest in the work.

Summary

The character table for rock-salt derived from the theory of groups applied to the unit cell containing four atoms of sodium and four atoms of chlorine,

gives eight triply degenerate normal modes of vibrations. One of them corresponds to the translations of the cell as a whole, two are infra-red active and Raman inactive, and five are inactive both in the Raman and the infra-red. The overtones of the latter five modes should however, appear in the Raman effect. This analysis of the vibration spectrum of the rock-salt structure gives a complete explanation of the infra-red absorption spectra of the alkali halides observed by Barnes and the Raman spectrum of rock-salt obtained by Fermi and Rasetti. The two infra-red absorption maxima at 161 and 247 $cm.^{-1}$ are taken as the two fundamental frequencies and the five frequencies at 228, 272, 298, 346 and 366 $cm.^{-1}$ identified from the Raman spectrum reproduced by Fermi and Rasetti, are assumed to be the first overtones of the remaining five frequencies of the lattice. The latter also shows three broad bands with peak frequencies of 81, 42 and 20 $cm.^{-1}$ These are shown to be the octaves of the superlattice frequencies of the second, third and fourth orders.

A general expression is derived for the thermal energy of cubic crystals of the rock-salt type in terms of the lattice and superlattice frequencies. The expression is evaluated for rock-salt and sylvine for a wide range of temperatures which in the case of sylvine is 3° to 285° absolute. Two of the lattice frequencies for sylvine are given by the infra-red spectrum and the others are deduced from those of rock-salt. The calculated values in either case are in reasonable agreement with experimental data, showing that the thermal energy of crystalline solids is satisfactorily explained on the basis of the ideas indicated in the foregoing paper by Sir C. V. Raman and developed further in the present communication.

REFERENCES

1. Venkateswaran, C. S. .. *Proc. Ind. Acad. Sci.*, A, 1941, **14**, 426.
2. Barnes and Czerny .. *Zeit. f. Physik*, 1931, **72**, 447.
3. Barnes .. *Ibid.*, 1932, **75**, 723.
4. Schæfer and Matossi .. *Das Ultrarot Spektrum*, Berlin, Julius Springer, 1930.
5. Schæfer .. *Zeit. f. Physik*, 1929, **54**, 153.
6. Krishnamurti .. *Ind. Jour. Phys.*, 1930, **5**, 105.
7. Fermi and Rasetti .. *Zeit. f. Physik*, 1931, **71**, 689.
8. Bhagavantam and Venkatarayudu .. *Proc. Ind. Acad. Sci.*, A, 1939, **9**, 224.
9. Venkateswaran, C. S. .. *Ibid.*, 1938, **8**, 448.
10. Keesom and Clark .. *Physica*, 1935, **2**, 698.
11. Southard and Nelson .. *Jour. Amer. Chem. Soc.*, 1933, **55**, 4865.
12. Blackman, M. .. *Proc. Roy. Soc.*, A, 1935, **148**, 365; **149**, 117.
13. Kellermann .. *Ibid.*, A, 1941, **178**, 17.
14. Clausius, Goldman and Perlick .. *Cf.* Keesom, *Phys. Zeit.*, 1934, **35**, 935.

STUDIES IN THE CYCLOHEXANE SERIES

PART V. The Isomeric 1-Carboxy-4-, and 3-Methylcyclohexane-1-α-Benzylacetic Acids

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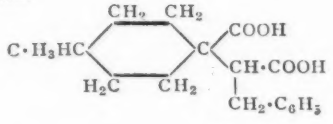
IN previous parts of this series[1] we have described the synthesis of the isomeric 1-carboxy-alkylcyclohexane-1-acetic acids, 1-carboxy-3: 3-dimethylcyclohexane-1-acetic acid, and 1-carboxy-alkylcyclohexane-1-succinic acids, but no indication was obtained of the isomerism connected with the multiplanar forms of the cyclohexane ring. The reason may be due to the small energy required to change the *boat* form of the cyclohexane ring into the *arm-chair* form. If this energy difference between the two forms is increased by suitable substitution, it may be possible to isolate them as definite entities.

We have, therefore, synthesised 1-carboxy-4-methylcyclohexane-1-α-benzylacetic acid (I) by the hydrolysis of ethyl-1-cyano-4-methylcyclohexane-1-α-benzylcyano-acetate (II) which is readily obtained by the benzylation of ethyl-1-cyano-4-methylcyclohexane-1-cyanoacetate, prepared by the condensation of the cyanohydrin of 4-methylcyclohexanone with ethyl sodio-cyanoacetate. The acid (I) was isolated in two isomeric forms, which were characterised by the preparation of their anhydrides, anilic acids, and imides. A similar pair of isomeric acids was obtained from the benzylation product of the sodio-derivative of ethyl-1-cyano-3-methylcyclohexane-1-cyanoacetate.



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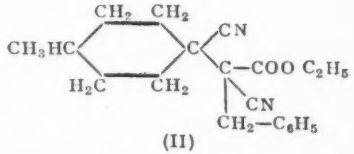

(II)

The results obtained by us in the present investigation can be interpreted on the assumption of the uniplanar form of the cyclohexane ring. No unequivocal chemical evidence has so far been adduced in favour of the strainless forms of this ring. Qudarati Khuda[2] claimed to have isolated the four isomeric forms of 1-carboxy-4-methylcyclohexane-1-acetic acid, and argued this as an evidence in favour of the multiplanar forms of the cyclohexane ring. Subsequent investigations, however, by us (*loc. cit.*), as well

as Goldschmidt and Gräfinger[3] have been unable to substantiate these claims. Moreover, 1-carboxy-4: 4-dimethylcyclohexane-1: 1-diacetic acid has been shown by us[4] as well as Roger Adams and Miller[5] to exist in one form only. Qudarati Khuda and his co-workers[6] have also described the isolation of 1-carboxy-3-methylcyclohexane-1-acetic acid and 1-carboxy-2-methylcyclohexane-1-acetic acid in four isomeric forms, contradictory to the observations of Desai, Hunter, Khan and Sahariya (*loc. cit.*), but the repetition of this work by one of us (R.D.D.) according to the details of the authors has shown that the alleged four forms do not exist, and that it is not possible to isolate each of the acid in more than two isomeric forms. Thus the claims of Qudarati Khuda and his co-workers are unconfirmed, and the conclusive chemical evidence in favour of the cyclohexane ring is yet wanting.

Experimental

1-Carboxy-4-methylcyclohexane-1-α-benzyl-acetic acids. Benzylation of Ethyl-1-cyano-4-methylcyclohexane-1-cyanoacetate.—1-Cyano-1-hydroxy-4-methylcyclohexane (32 g.) was gradually added to ethyl sodiocyanoacetate (Na = 5·3 g.; alcohol = 60 c.c.; ethyl cyanoacetate = 28·5 g.), and the mixture was allowed to remain at the room temperature for 48 hours. The mixture was kept at the same temperature for further two days after the gradual addition of benzyl chloride (29 g.), and then heated on the water-bath under reflux for 24 hours. After the recovery of alcohol, the residue was added to a large quantity of water, and the precipitated viscous mass was extracted with ether, dried, recovered and distilled, giving a fraction b.p. upto 125°/6 mm., a fraction b.p. 125–200°/6 mm., and ethyl-1-cyano-4-methylcyclohexane-1-α-benzylcyanoacetate b.p. 230–234°/6 mm. The first fraction was rejected, while the second fraction (14 g.) was rebenzylated in presence of sodium ethoxide (benzyl chloride = 8 g., Na = 1·4 g.; absolute alcohol = 15 c.c.), and the product was worked up as already described. The total yield was 30 gm. Some undistillable residue crystallising from alcohol in white, thick plates (m.p. 143°) was left in the Claisen flask, and was identified as *1-cyano-4-methylcyclohexane-1-α-benzyl-acetonitrile* as it gave 1-carboxy-4-methylcyclohexane-1-α-benzyl-acetic acid (B) (m.p. 195°) described below. [Found: C, 80·8; H, 8·0; $C_{17}H_{20}N_2$ requires C, 80·9; H, 7·9 per cent.]

The Dicyano-benzyl-acetic ester was a straw-coloured, viscous liquid which solidified to a glassy mass, and crystallised from dilute alcohol in white plates (m.p. 84–92°.) [Found: C, 73·9; H, 7·4; $C_{20}H_{24}O_2N_2$ requires C, 74·0; H, 7·4 per cent.]

Hydrolysis of the ester.—The ester (25 g.) was kept in contact with concentrated sulphuric acid (50 c.c.) overnight and water (66 c.c.) then added.

The mixture was heated for 24 hours, diluted with water, cooled and extracted with ether. The ethereal extract was shaken with aqueous sodium carbonate (10%); when the alkaline solution was acidified with concentrated hydrochloric acid, a mixture of acids separated. After saturation of the liquid with ammonium sulphate, the acids were extracted with ether, dried and recovered. As the residue did not solidify because of its contamination with the anhydride formed during the hydrolysis, it was heated with dilute caustic soda solution, filtered, and acidified. The cold solution which deposited some solid acid was extracted with ether, dried, and the acids recovered. The crude solid (m.p. 150–62°) was treated with warm benzene, when a portion of it dissolved leaving a solid (m.p. 180–82°). This acid (A) crystallised from dilute alcohol in white, lustrous needles (m.p. 183°) (effer.). [Found: C, 70·1; H, 7·5; $C_{17}H_{22}O_4$ requires C, 70·3; H, 7·5 per cent.]

The benzene mother-liquor gave a solid m.p. 98–106° on evaporation. This was rehydrolysed with concentrated hydrochloric acid for 12 hours, and the acids worked up in the usual manner. Extraction with warm benzene gave a further amount of the sparingly soluble acid (A), while the mother-liquor on concentration gave another isomeric *acid* (B) (m.p. 190–92°). It crystallised from dilute alcohol in colourless, thick plates (m.p. 195°), and depressed to 165° by the acid (A). The amount of this acid was small, but some more of the same acid was obtained from the *dinitrile* which was left in the distillation flask. The ratio of the acid A : B was 10 : 1. [Found: C, 70·2; H, 7·9; $C_{17}H_{22}O_4$ requires C, 70·3; H, 7·5 per cent.]

Derivatives of the Acid (*A*) (*m.p.* 183°):—

The Anhydride prepared by heating the acid in an oil-bath at 165–70° for three hours crystallised from hexane in long, white needles (m.p. 115°). [Found: C, 75·0; H, 7·4; $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·3 per cent.]

The Anilic acid prepared by mixing the anhydride (0·3 g.) and aniline (0·3 g.) in benzene solution crystallised from dilute alcohol in needles (m.p. 165°). [Found: C, 73·5; H, 7·4; $C_{23}H_{27}O_3\ N \cdot \frac{1}{2}\ H_2O$ requires C, 73·8; H, 7·5 per cent.]

The Imide obtained by heating the dry ammonium salt of the acid at 180° for three hours crystallised from dilute alcohol in clusters of white needles (m.p. 181°). [Found: C, 74·8; H. 7·9; $C_{17}H_{21}O_2\ N$ requires C, 75·1, H, 7·8 per cent.]

The calcium and barium salts of the acid were soluble in water while the lead and copper salts were insoluble.

Derivatives of the Acid (B) (m.p. 195°):—

The Anhydride obtained by heating the dry acid at 165–70° for three hours crystallised from hexane in needles (m.p. 109°) (depressed to 93–94° by the anhydride A). [Found: C, 74·9; H, 7·5; $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·3 per cent.]

The Anilic acid crystallised from dilute alcohol in white needles (m.p. 175°) (depressed to 151° by the anilic acid A). [Found: C, 73·4; H, 7·5; $C_{23}H_{27}O_3N \cdot \frac{1}{2} H_2O$ requires C, 73·8; H, 7·5 per cent.]

1-*Carboxy*-3-*methylcyclohexane*-1-*α-benzyl acetic acids.*—Ethyl-1-cyano-3-methylcyclohexane-1-cyanoacetate, prepared from freshly distilled 1-cyano-1-hydroxy-3-methylcyclohexane (20 g.) ethyl cyanoacetate (18 g.) and sodium ethoxide (3·2 g. of sodium and 40 c.c. of absolute alcohol) was kept for 48 hours and treated with benzyl chloride (20 g.). The ester was obtained as a viscous oil which was extracted in ether, dried, recovered and distilled, giving a fraction b.p. upto 125°/8 mm., a fraction b.p. 130–200°/8 mm., and ethyl-1-cyano-3-methylcyclohexane-1-*a*-benzylcyanoacetate, b.p. 237–39°/8 mm., which solidified to a hard, glassy mass. The first fraction was rejected while the second fraction (24 g.) was re-treated with benzyl chloride (12 g.) in presence of sodium ethoxide (2·3 g. of sodium and 30 c.c. of absolute alcohol). The total yield of the *dicyanobenzylaceteic ester* was 20 gm. It crystallised from dilute alcohol in clusters of thick plates (m.p. 95–105°). [Found: C, 73·6; H, 7·4; $C_{20}H_{24}O_2N_2$ requires C, 74·0; H, 7·4 per cent.]

Hydrolysis of the ester.—The ester (20 g.) was hydrolysed as usual, and as the crude mixture of acids isolated by ether did not solidfy owing to the presence of some anhydride it was heated with 10 per cent. NaOH for half an hour, and the acids recovered as usual after acidification with concentrated hydrochloric acid. The crude mixture (m.p. 60–120°), on trituration with warm benzene left a solid (m.p. 180–82°), which recrystallised from dilute alcohol in needles (m.p. 184°) and was identified as 1-*carboxy*-3-*methyl-cyclohexane*-1-*α-benzyl-acetic acid* (*A*). [Found: C, 69·8; H, 7·6; $C_{17}H_{22}O_4$ requires C, 70·3; H, 7·5 per cent.]

Its calcium and barium salts were soluble in hot as well as cold water, while the lead and copper salts were insoluble. The benzene mother-liquor was concentrated, and some more of the acid (A) was obtained. On further concentration of the mother-liquor, a fraction (m.p. 165–68°) was deposited. It recrystallised from dilute alcohol in white, tiny needles (m.p. 178°) (depressed to 165° by the acid A) and was the *isomeric acid* (*B*). The proportion of A : B was 10:1. The two isomeric acids were similar in the solubilities of their

lead, copper, calcium and barium salts. [Found: C, 70·1; H, 7·8; $C_{17}H_{20}O_4$ requires, C, 70·3; H, 7·5 per cent.]

Derivatives of the Acid (*A*) (*m.p.* 184°):—

The Anhydride prepared by heating the dry acid at 165–70° for three hours crystallised from hexane in plates (m.p. 102°). [Found: C, 74·8; H, 7·6; $C_{17}H_{20}O_3$ requires C, 73·0; H, 7·3 per cent.]

The Anilic acid crystallised from dilute alcohol in tiny needles (m.p. 152°). (Found: C, 75·3; H, 7·5; $C_{23}H_{27}O_3$ N requires C, 75·6; H, 7·3 per cent.)

The Imide crystallised from dilute alchol in needles m.p. 165–166°. [Found: C, 74·9; H, 8·0; $C_{17}H_{21}O_2N$ requires C, 75·1; H, 7·8 per cent.]

Derivatives of the Acid (*B*) (*m.p.* 178°):—

The Anhydride obtained by heating the dry acid at 170° for three hours crystallised from hexane in white needles (m.p. 130°). [Found: C, 74·6; H, 7·4; $C_{17}H_{20}O_3$ requires C, 75·0; H, 7·3 per cent.]

The Anilic acid crystallised from dilute alcohol in white, lustrous needles (m.p. 170°). [Found: C, 75·4; H, 7·4; $C_{23}H_{27}O_3$ N requires C, 75·6; H, 7·3 per cent.]

Summary

Benzylation of the sodio-derivative of ethyl-1-cyano-4-methyl-cyclohexane-1-cyanoacetate yields a dicyano ester, which gives a pair of isomeric 1-carboxy-4-methylcyclohexane-1-α-benzylacetic acids on hydrolysis. Similar pair of isomeric 1-carboxy-3-methylcyclohexane-1-α-benzylacetic acids has been also obtained. These results can equally be interpreted on the uniplanar form of the cyclohexane ring.

REFERENCES

1. Desai, Hunter and co-workers .. *J.*, 1936, 416, 1162; 1939, 84.
2. Qudarati Khuda .. *J. Ind. Chem. Soc.*, 1931, **8**, 277.
3. Goldschmidt and Gräfinger *Ber.*, 1935, **68**, 279.
4. Desai, Hunter and Sahariya *Nature*, 1936, **138**, 548.
5. Roger Adams and Miller .. *J. Amer. Chem. Soc.*, 1936, **58**, 787.
6. Qudarati Khuda and co-workers *J. Ind. Chem. Soc.*, 1938, **15**. 462, 489.

RAMAN SPECTRUM OF MERCURIC CHLORIDE IN RELATION TO ITS STRUCTURE

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1. *Introduction*

The experimental determination of the relative positions in space of the atoms in a molecule, can now be effected by a variety of methods. Diffraction of X-rays by solids, diffraction of electrons by vapours, measurement of dipole moments, absorption spectra and Raman spectra in different states of aggregation are among the most important ones. A study of the structure of mercuric chloride, from some of the aspects stated above, has been undertaken by many earlier investigators.

Braekken and Scholten[1] concluded, from studies on X-ray diffraction, that $HgCl_2$ crystallises in the rhombic class with four molecules in the unit cell, the space group being V_h^{16}. According to them, the structure is molecular and the atoms in each molecule are collinear. Braune and Knoke[2] determined the nuclear distances of $HgCl_2$ by the electron diffraction method. Greg[3] also undertook a detailed study of the structure of mercury halides by the electron diffraction method and concluded that it is not possible to uniquely determine the configuration of the mercuric chloride and bromide owing to the relatively small scattering powers of the atoms attached to the mercury atom. These authors expressed the opinion that their results are, on the whole, in agreement with a linear structure for the molecule. The dipole moment of mercuric chloride, calculated by Bell[4] from solubility data, is 4×10^{-18}. Curran and Wenzke[5] determined the same, using dioxane as solvent and found it to be $1{\cdot}29 \times 10^{-18}$. As the value is quite appreciable, the authors conclude that the configuration of mercuric chloride is not linear. On the contrary, Braune and Linke[6] determined the dielectric constant of $HgCl_2$ at temperatures between 320° C. and 430° C. and found the molecular polarisation to be independent of temperature. This shows that the molecule has no dipole moment and has therefore to be linear.

Krishnamurty[7] studied the Raman spectrum of $HgCl_2$ in the form of crystalline powder. He recorded two lines 312 (strong) and 381 (weak). As the spectrum resembles those of CO_2 and CS_2, he suggested a linear model for the $HgCl_2$ molecule. The presence of the weak line is explained as due

to the oscillation of one of the chlorine atoms against the remaining group (HgCl). This explanation is, however, open to serious objections. He also examined a very concentrated solution of mercuric chloride in CH_3OH. The line is symmetrically broadened and slightly displaced (319). The broadening observed is explained as due to the increased rotational freedom of the molecules in the dissolved state. Braune and Engelbrecht[8] found that $HgCl_2$, dissolved in water, gives a strong line at 320 cm.$^{-1}$ and in acetic ester gives a line at 332 cm.$^{-1}$ They also studied the Raman spectrum in the molten and vapour states. Molten $HgCl_2$ gives a strong and broad line at 314 cm.$^{-1}$ and a very weak line at 376 cm.$^{-1}$ In the gaseous state the principal line, according to these authors, shifts to 355 cm.$^{-1}$ The variation of Raman frequencies, as we pass from the liquid or solid state to the gaseous state, is a characteristic of polar molecules. So the obvious conclusion to be drawn from the above result, is that $HgCl_2$ is polar and hence, a bent molecule.

The existence of strong Raman lines in $HgCl_2$ is an outstanding evidence that the link in the molecule is covalent. Sidgwick and Powell[9] collected the experimental evidence as to the stereochemistry of polyvalent atoms and tried to relate it to the simplest expression of electronic structure, the size of the valency groups and the number of shared electrons they contain. They generalised that the structure is always linear when the valency group is less than 8 with a covalency of 2. As $HgCl_2$ belongs to this category, it should be expected to be linear.

From what has been said in the foregoing paragraphs, it will be seen that evidence, available from different branches of investigation in the matter of the structure of $HgCl_2$, is conflicting. In some cases, different authors, working in the same branch, have arrived at different conclusions. It is very important that the structure of $HgCl_2$ should be definitely established and the discrepancies reconciled.

In the present paper, the author has made a detailed study of the different aspects of the Raman spectrum method. The results are presented and discussed with special reference to the structure of $HgCl_2$.

2. *Experimental Technique*

The following technique is adopted for obtaining a good specimen of the solid suitable for Raman spectrum studies. The substance is contained in a pyrex glass tube and is melted by means of cylindrical electric heater surrounding the tube. The substance is then slowly cooled down to the room temperature by reducing the current in the heater. In this way, a reasonably transparent solid lump is obtained in the glass tube. The tube is cautiously broken and a single transparent crystal of size 1 cm. $\times$ 1 cm. $\times$ 1·5 cm. is obtained from the lump. Two of its faces, one for illumination and the other for

observation, are ground and polished. The specimen of a single crystal so prepared is used in the present investigation.

For obtaining the Raman spectrum in the liquid state, a pyrex glass tube of $\frac{3}{4}''$ diameter, flattened at one end and drawn out at the other into the shape of a horn, is used as the container. A cylindrical heater, open at either end, and provided with a window 6 cm. $\times$ 2·5 cm. in its body, lengthwise, for the purpose of illumination has been constructed. The Raman tube is supported longitudinally inside the heater by means of two brass discs. A thermometer is inserted and suitable arrangements are made for preventing parasitic light from entering the spectrograph.

To get the polarisation characters of the lines, the horizontal and vertical components are simultaneously photographed interposing a suitably oriented double-image prism in the track of the scattered light. A set of intensity marks is given on the same plate by the method of varying slit-widths. A standard quartz globe tungsten ribbon lamp is used as the source. A steady current of 14·8 amperes is maintained in the lamp by feeding it from a battery of 220 volts. In calculating the polarisation characters, one must take into account several sources of error. The polarisation characters of the Raman lines of CCl_4 are determined with the same arrangement and the correction term necessary to bring the depolarisation factors of the lines 218 cm.$^{-1}$ and 312 cm.$^{-1}$ to 86%, is calculated. In this manner, it is found that the various errors are corrected for, if the observed value for the instrument employed in the present investigation is reduced to 56% of itself.

For purposes of studying the Raman spectrum in the dissolved state, pure recrystallised sample of the substance is dissolved in methyl alcohol which is purified by distillation over calcium. The concentrated solution, which is of about 30% by weight of $HgCl_2$, is filtered through several thicknesses of filter-paper two or three times and finally filtered into the Raman tube. The spectrum is photographed by the usual arrangement for liquids.

A special container, consisting of a thick-walled pyrex tube of diameter 3 cm. and length 23 cm., has been used for studying the Raman spectrum of this substance in the vapour state. A few crystals of $HgCl_2$ are contained in the tube which is sealed off after evacuation. The tube is heated, in the furnace already described, to a temperature of about 300° C. and an exposure of about 100 hours has been found necessary for recording the Raman spectrum in the vapour state.

In all cases, the light from a six-inch quartz mercury lamp is focussed on to the container or the substance by means of a large glass condenser and a Fuess glass spectrograph having a high light-gathering power has been used. Wherever necessary, suitable filters have been used in the path of the incident beam to effectively cut off the continuous spectrum in the incident light.

3. *Results*

The following table gives the Raman shifts in solid $HgCl_2$. The numbers in the brackets represent the relative intensities.

TABLE I

Exciting line A.U.	Wavelength of the Raman line A.U.	Frequency cm.$^{-1}$	Raman shift cm.$^{-1}$
4358	4431·4	22560	378 (0)
,,	4418·7	22625	313 (10)
,,	4299·9	23251	−313 (3)
4078	4130·8	24202	314 (2)
4047	4098·8	24391	314 (8)
,,	4067·0	24581	124 (2)
,,	4062·2	24610	95 (1)
,,	4058·5	24633	72 (3)
,,	4034·7	24778	− 73 (2)
,,	4026·6	24823	−123 (1)
,,	3995·9	25019	−314 (2)

$\Delta\ \nu = 73, 95, 124, 314, 378$

The spectrogram is reproduced in Plate XXXV. The lines 73, 95 and 124 are recorded for the first time.

Table II gives the results obtained with the liquid.

TABLE II

Exciting wavelength A.U.	Wavelength of the Raman line A.U.	Frequency cm.$^{-1}$	Raman shift cm.$^{-1}$
4358	4431·2	22561	377 (1)
,,	4423·2	22602	336 } 315 (10)
,,	4414·7	22645	293 }
4348	4406·3	22688	307 (1)
4358	4302·8	23234	−296 } −319 (5)
,,	4294·3	23280	−342 }
4348	4289·1	23308	−313 (0)
4078	4130·9	24261	315 } 304 (2)
,,	4127·0	24224	292 }
4047	4102·4	24369	336 } 318 (8)
,,	4096·2	24405	300 }
4078	4027·6	24822	−316 (0)
4047	3997·8	25007	−302 } −318 (2)
,,	3992·6	25039	−334 }

$\Delta\ \nu = 314, 377$

The breadth of the strong line is about 40 cm.$^{-1}$ The two edges of the line are measured and the Raman shift is taken as the mean of these two frequencies. A microphotometric record showing the comparative structures of the solid line and the liquid line is reproduced in the Plate.

Table III contains the results obtained in a solution of $HgCl_2$ in CH_3OH and in the $HgCl_2$ vapour.

TABLE III

State	Exciting wavelength A.U.	Wavelength of the Raman line A.U.	Frequency cm.$^{-1}$	Raman shift cm.$^{-1}$
Solution ..	4358	4420·1	22618	320
Vapour ..	4047	4098·0	24395	310

The frequencies obtained by the author are in agreement with those obtained by earlier investigators except in the case of gas. This result is very significant and is discussed later on.

The polarisation values obtained in the liquid state are as follows: 314 (51%); −314 (52%) and 376 (P). The above values are corrected for the various errors as mentioned before. As the second line is very weak it is not possible to actually measure the depolarisation factor, but it is found that it is also polarised.

4. Discussion of Results in Relation to Structure

As has already been mentioned there are two possibilities to be considered namely: (i) a linear configuration and (ii) a bent one for the mercuric chloride molecule. The point group of the symmetrical molecule is $D_{\infty h}$ and such a structure should give rise to one polarised Raman line. The bent structure comes under the point group C_{2v} and should accordingly give rise to three Raman lines, two of which should be well polarised and the third one, usually of the highest frequency should be depolarised to the limit. As mercuric chloride gives rise to two lines, it is difficult to decide between these two alternatives by studying the number of Raman lines only. Nevertheless, it can be argued that since the line 314 is very strong, the other two lines, which should be present if $HgCl_2$ is a bent molecule, should be sufficiently intense compared to the intensity of the strong line 312. The extreme weakness of one line 318 and the non-existence of the other line suggest that it is not a bent molecule. This view is confirmed by the following considerations.

In the case of polar molecules such as SO_2, HCl, etc., there are large variations in the frequencies in different states of aggregation. On the other hand, in the case of $HgCl_2$, there are practically no variations. The early results of Braune and Engelbrecht show a large variation in liquid and gaseous states, the frequency in the liquid state being 314 and that in the gaseous state 356. They accordingly concluded that $HgCl_2$ is a polar molecule and

hence a bent one. Contrary to these observations, the results of the present investigation show the frequency, which is 314 in the solid and the liquid states, is 310 in the gaseous state. The very small variation of 4 wave numbers is not of much significance. The two frequencies are practically identical in the solid and the liquid states. In the solution there is a very small shift to the longer wavelength side. So we can conclude that there are no marked variations of frequencies in different states. Hence $HgCl_2$ should be non-polar and therefore, a linear molecule.

There is yet another line of reasoning which shows that it is a linear molecule. In the case of the bent molecule, we shall designate the parallel symmetrical vibration by ν_1, the parallel deformation vibration by ν_2 and the asymmetric perpendicular vibration by ν_3. ν_1 and ν_2 should be polarised and ν_3 depolarised. Accordingly, SO_2 gives three lines at 526, 1146 and 1340. 1340 has been found to be depolarised to the limit. In the present case the strong line 314 may be identified with ν_1. ν_3 should be on the longer wavelength side of ν_1 and should be depolarised. If we identify 378 with ν_3, it should be depolarised in case the molecule is bent. But the results obtained in this investigation show that 378 is polarised. Hence, the polarisation values do not fit in with a bent model. The considerable depolarisation of the total symmetric line is due to the broadening of the line which may presumably be identified with rotational scattering. The weak line in $HgCl_2$ is polarised as in the case of 798 in CS_2 and 1285 in CO_2. Hence this may be identified with the overtone of the forbidden frequency as in the case of CO_2 and CS_2. Raman effect data of $HgCl_2$ strongly support the view that the molecule is linear.

5. *Some Special Features*

Good Raman spectra of the solid and the liquid are obtained in the present investigation. The plates are run through a Moll microphotometer and the relative intensities of the Stokes and anti-Stokes components are obtained in the usual way with the help of intensity marks recorded on each plate. Results are given in Table IV.

TABLE IV

State	Temp. °C.	Frequency	$\frac{I_S}{I_{A.S.}}$ Obs.	$\frac{I_S}{I_{A.S}}$ Calc.
Solid ..	29	314	3·8	4·0
Liquid ..	280	314	1·6	2·0

It is evident from the above table that the observed value is in agreement with the value calculated in the case of the solid. The agreement between the

observed and the calculated values is not very satsifactory in the liquid presumably because the liquid is slightly yellowish and the results are not corrected for absorption.

The principal line is considerably broadened in the liquid state and has acquired an unsymmetrical distribution of intensity. A satisfactory explanation of this interesting phenomenon is at present difficult to furnish. It may be suggested that, as the temperature is very high, a good proportion of molecules, excited to different vibrational states, may be expected to be present. The vibrational frequencies, arising from such molecules, may be expected to give rise to a broad band of a composite character. Other issues such as the increased freedom of rotation at high temperatures, may also have to be taken into account. This is suggested by the fact that the band, as a whole, exhibits considerable depolarisation. It may be added here that the line, observed in the crystal, is quite sharp as may be expected.

In the Raman spectrum of the solid, three low frequency lines have been recorded here for the first time. These three lines at 73, 95 and 124 $cm.^{-1}$ are to be explained as due to lattice oscillations. From the crystal structure, it is clear that we should expect a number of lines in this region because there are four molecules per unit cell. A detailed correlation of the crystal structure with the observed lattice spectrum is not attempted here. The large intensity of the lattice lines is, however, in accordance with the proposed linear structure and the consequent marked optical anisotropy of the molecule. These three lines may provisionally be ascribed to modes of oscillation in which the molecule, as a whole, tilts about various axes. Such an assignment receives some support from the fact that these lines do not persist in the liquid state. It may, however, be remarked here that Sponer and Teller[10] have recently indicated that the frequency at 70, as obtained from a study of the electronic spectra, may be ascribed to the transverse vibration of the $HgCl_2$ molecule.

The three lattice lines, which appear in the Raman spectrum of solid $HgCl_2$, are absent in the liquid state. This is natural because the lattice lines are characteristic of only the solid state. The Raman spectrum of the liquid exhibits, besides the vibrational Raman lines, unresolved wing in the neighbourhood of the Rayleigh line. The distribution of intensity in the wing is also studied in the present investigaion. λ 4358 A.U. is selected as the exciting line and the results are given in Table V.

TABLE V

$\Delta\nu$	9	18	27	36	45	54	63	72	81	90	99	108	117	123
I	1318	224	170	132	120	96	87	79	63	60	44	37	29	25

It may be noted that the wing starts with a maximum intensity very near the Rayleigh line and gradually diminishes till it becomes negligible at a distance of about 100 cm.$^{-1}$ Thus the wing in liquid $HgCl_2$ possesses all the characters that are typical of the wing usually obtained in common liquids.

6. *Summary*

In this paper an attempt is made to gather as much evidence as possible from different aspects of the Raman spectrum method for the purpose of determining the structure of $HgCl_2$.

Raman spectra in the solid, liquid, gaseous and dissolved states are obtained. The solid gives lines at $\Delta\nu$: 73, 95, 124, 314, 378 cm.$^{-1}$ The liquid gives lines at $\Delta\nu$: 314, 377 and exhibits a prominent wing alongside the Rayleigh lines. The three low frequency lines, obtained in the solid state, have been observed for the first time and are explained as due to the lattice oscillations. The principal Raman line $\Delta\nu = 314$ cm.$^{-1}$ is found to occur in the same position in the gaseous and the dissolved states also. The constancy of the Raman frequency in all the states of aggregation, is a characteristic of non-polar molecules. Hence it is concluded that $HgCl_2$ should be non-polar and therefore, a linear molecule.

A study of the polarisation characters of the Raman lines in the liquid state reveals that both the Raman lines are polarised. The occurrence of the two lines and their polarisation characters are explained on the basis of a linear structure. The strong line 314 cm.$^{-1}$ is attributed to the total symmetric oscillation and 377 cm.$^{-1}$ is explained as the overtone of the forbidden frequency.

Incidentally, other prominent features of the Raman spectrum of $HgCl_2$ such as the breadth characters of the lines, etc., at different temperatures are noted and dealt with.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam for the keen interest he has shown during the progress of this investigation.

REFERENCES

1. Braekken and Scholten .. *Z. Kristal.*, 1934, **89**, 448.
2. Braune and Knoke .. *Z. Phys. Chem.*, 1933, B **23**, 163.
3. Greg .. *Trans. Far. Soc.*, 1937, **33**, 852.
4. Bell . *Jour. Chem. Soc.*, 1931.
5. Curram and Wenzke .. *Jour. Amer. Chem. Soc.*, 1935, **57**. 2162.
6. Braune and Linke .. *Z. Phys. Chem.*, 1935, B **31**, 12.
7. Krishnamurty .. *Ind. Jour. Phys.*, 1930, **5**, 105; **6**, 113; and *Nature*, 1930, **125**, 892.
8. Braune and Engelbrecht .. *Z. Phys. Chem.*, 1930, **10** B, 1; 1932, **19** B, 303.
9. Sidgwick and Powell .. *Proc. Roy. Soc.*, 1940, **176**, 153.
10. Sponer and Teller .. *Rev. Mod. Phys.*, 1941, **13**, 75.

Raman Spectra of Mercuric Chloride

EFFECT OF TEMPERATURE ON THE INTENSITIES OF RAMAN LINES

Part I. Crystals

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1. Introduction

As early as 1928, Krishnan[1] pointed out that in the Raman spectrum of liquid CCl_4, the Stokes lines become weaker and the anti-Stokes lines stronger with increase of temperature. Later, Ananthakrishnan[2] studied the Raman spectrum of liquid CCl_4 over an interval of temperature extending from 25° to 200° C. and showed that the integrated intensities of the Stokes lines in CCl_4 do not increase with increasing temperatures.

Birckwedde and Peters[3] investigated the Raman spectrum of crystalline quartz between 180° C. and 550° C. and concluded that the Stokes lines become weaker at higher temperatures. Landsberg and Mandelstamm[4] reinvestigated the case of quartz and observed that the intensity of the Stokes line at 465 cm.$^{-1}$ increased in the ratio 1 : 1·29 when the temperature was raised from 295° K. to 810° K.

Recently Ornstein and Went[5] studied the influence of temperature on the Raman lines of crystalline quartz and calcite over a range extending from 90° K. to about 420° K. Some of the important conclusions derived from their experimental investigations are (i) the ratios of intensities of the Stokes and the anti-Stokes lines are in conformity with the theoretically calculated values; (ii) the absolute intensities of the Stokes lines showed marked decrease with rise of temperature; and (iii) the observed decrease in intensity is more pronounced for the lower frequencies.

From the above survey of the experimental work carried out so far in this line of investigation, it is clear that the results obtained in the case of liquids are very meagre and qualitative and that the results obtained in crystals by different authors are at variance with one another. In view of the above facts, it is considered desirable to take up a detailed investigation of the influence of temperature on the intensities of Raman lines both in solids and

liquids. Some of the results obtained in the case of a few typical crystals are presented in this paper.

2. *Experimental Arrangements*

Light from a 6-inch quartz mercury arc lamp is condensed by means of an 8-inch glass condenser on to one face of the crystal and the scattered light emerging out of one of the other faces of the crystal is focussed on the slit of a two-prism glass spectrograph of high light-gathering power. In the case of quartz a cut and polished one-inch cube has been used and the other two crystals, sodium nitrate and mercuric chloride, are grown and polished in this laboratory. With suitable precautions, intense and clear spectrograms showing the Stokes and anti-Stokes lines have been obtained.

A specially constructed electric heater was made to surround the crystal. A mount of oxidised copper foil, prepared carefully so as to give a uniform dull-black surface, is used for mounting the crystal. A thermometer kept in contact with the crystal indicated the temperature within an accuracy of $\pm$ 5° C. With such an arrangement, the Raman spectra of each crystal at different temperatures have been obtained side by side under exactly identical conditions. Great care has been taken to see that the time of exposure and the intensity of the source are kept constant while obtaining the Raman spectra of the same crystal at different temperatures.

A set of intensity marks is recorded on each plate by the method of varying slit-widths using the continuous radiation emitted by a standard quartz globe tungsten ribbon lamp as the source. The plates are run through a Moll Microphotometer and the densities of the various lines are obtained. The density-log.-intensity curves are drawn for each wavelength at which the various Raman lines that are to be compared with each other appear. The intensity of any line as a fraction of the standard radiation having the same wavelength as the line itself is read from the above curves and the intensities of the Stokes and the anti-Stokes lines are computed from a knowledge of the energy distribution in the radiation emitted by the lamp. Since the crystals are perfectly colourless and not very large, no correction need be made on the score of absorption.

As the lines chosen for investigation in the various crystals do not show any appreciable variation in their breadth characters with change of temperature, within the range employed, only the peak intensities are noted and compared.

3. *Results*

Tables I, II and III contain the results relating to the effect of temperature on the intensities of Stokes lines in crystalline quartz, sodium nitrate

and mercuric chloride respectively. The results in column 4 of each of these tables are calculated with the help of relation (1) given in the next section and contained in Placzek's theory.

TABLE I

Quartz

$\Delta\nu$	Temp.	$\frac{I_T}{I_{308}}$ Obs.	$\frac{I_T}{I_{308}}$ Calc.	Quotient
465 cm.$^{-1}$	308° K.	1·00	1·00	1·00
	373	0·78	1·07	1·37
	473	0·64	1·17	1·83

TABLE II

Sodium Nitrate

$\Delta\nu$	Temp.	$\frac{I_T}{I_{308}}$ Obs.	$\frac{I_T}{I_{308}}$ Calc.	Quotient
1065 cm.$^{-1}$	308° K.	1·00	1·00	1·00
	378	0·81	1·02	1·26
	423	0·68	1·03	1·51
	493	0·58	1·05	1·81

TABLE III

Mercuric Chloride

$\Delta\nu$	Temp.	$\frac{I_T}{I_{308}}$ Obs.	$\frac{I_T}{I_{308}}$ Calc.	Quotient
315 cm.$^{-1}$	308° K.	1·00	1·00	1·00
	373	0·83	1·09	1·31
	423	0·73	1·17	1·60

Tables IV and V contain results relating to the effect of temperature on the anti-Stokes Raman lines. The results contained in column 4 of each of these tables are calculated with the help of relation (2).

TABLE IV
Quartz

$\Delta\nu$	Temp.	$\frac{I_T}{I_{308}}$ Obs.	$\frac{I_T}{I_{308}}$ Calc.	Quotient
	308° K.	1·00	1·00	1·00
− 465 cm.$^{-1}$	373	1·25	1·61	1·29
	473	1·52	2·46	1·62

TABLE V
Mercuric Chloride

$\Delta\nu$	Temp.	$\frac{I_T}{I_{308}}$ Obs.	$\frac{I_T}{I_{308}}$ Calc.	Quotient
	308° K.	1·00	1·00	1·00
− 315 cm.$^{-1}$	373	1·22	1·40	1·15
	423	1·35	1·73	1·28

Tables VI and VII contain results relating to the effect of temperature on the ratio of intensities of the Stokes and the anti-Stokes Raman lines in quartz and mercuric chloride.

TABLE VI
Quartz

$\Delta\nu$	Temp.	$\frac{h\nu_j}{e^{\frac{h\nu_j}{kT}}}$	$\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4 \frac{h\nu_j}{e^{\frac{h\nu_j}{kT}}}$	$\frac{I_S}{I_{A,S}}$ Obs.
	308° K.	8·72	7·42	7·68
465 cm.$^{-1}$	378	5·84	4·97	4·79
	473	4·10	3·48	3·25

TABLE VII
Mercuric Chloride

$\Delta\nu$	Temp.	$\frac{h\nu_j}{e^{\frac{h\nu_j}{kT}}}$	$\left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4 \frac{h\nu_j}{e^{\frac{h\nu_j}{kT}}}$	$\frac{I_S}{I_{A,S}}$ Obs.
	308° K.	4·34	3·89	4·12
315 cm.$^{-1}$	373	3·36	3·01	2·80
	423	2·91	2·61	2·25

4. *Discussion of Results*

The aggregate average intensity per molecule of the Stokes and the anti-Stokes lines has been obtained by Placzek and his results are given in (1) and (2) respectively.

$$I_{(\nu-\nu_j)} \propto (\nu-\nu_j)^4 \frac{1}{1-e^{\frac{-h\nu_j}{kT}}} \tag{1}$$

$$I_{(\nu+\nu_j)} \propto (\nu+\nu_j)^4 \frac{1}{e^{\frac{h\nu_j}{kT}}-1} \tag{2}$$

From (1) and (2), the ratio of the intensities of the Stokes and the anti-Stokes lines is obtained as in (3).

$$\frac{I_{(\nu-\nu_j)}}{I_{(\nu+\nu_j)}} = \left(\frac{\nu-\nu_j}{\nu+\nu_j}\right)^4 e^{\frac{h\nu_j}{kT}} \tag{3}$$

From the results given in Tables I, II and III it is obvious that the intensity of the Stokes lines, in all the three cases studied, decreases with rise in temperature. This is contrary to what is indicated by equation (1). The discrepancy between the theory and experiment both in magnitude and direction is clearly shown in Fig. 1 (*a*) for the case of quartz. Results contained in Tables IV and V show that the intensity of the anti-Stokes lines increases with rise of temperature as may be expected. It must, however, be remarked that the rate at which the intensity increases is not in conformity with that contained in the expression (2) and this discrepancy is illustrated graphically in Fig. 1 (*b*) for the case of quartz. The results given in Tables VI and VII on the other hand, show convincingly that, in spite of the sharp disagreement between experiment and theory that has been noticed in the matter of the individual intensities of the Stokes and the anti-Stokes lines, their ratio as observed at different temperatures is in conformity with the theory.

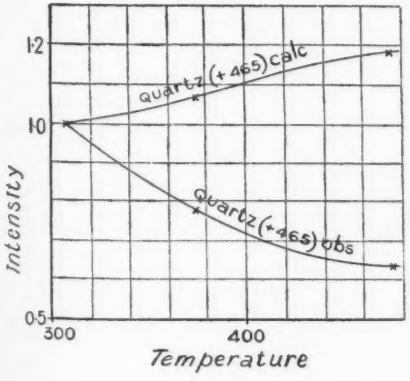

FIG. 1 (*a*)

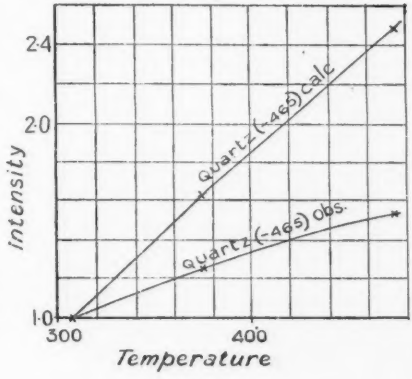

FIG. 1 (*b*)

It is the main purpose of this paper to draw attention to a failure of the existing theory in respect of the temperature dependence of the intensity of the vibrational Raman lines. The failure appears to be common to the lattice as well as the internal oscillations in crystals. These investigations will also be extended to liquids in due course. The weak point of the theory is in the assumption that molecules in the higher vibrational states, on account of the larger amplitudes involved, give rise to larger scattering moments. This point will be examined and discussed more fully after obtaining data in some typical liquids as well.

5. *Summary*

The dependence of intensity on temperature of the Raman lines, 465 in crystalline quartz, 315 in mercuric chloride, and 1065 in a sodium nitrate crystal, has been experimentally studied. Sharp disagreements with the existing theories have been noticed in the matter of the individual intensities of the Stokes and the anti-Stokes lines at different temperatures. The experimentally observed ratio of the intensity of the Stokes line to that of the corresponding anti-Stokes line at different temperatures conforms closely to what may be expected on the basis of the existing theories.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam under whose guidance this investigation has been taken up.

REFERENCES

1. Krishnan, K. S. .. *Nature*, 1928, **122**, 650.
2. Ananthakrishnan, R. .. *Proc. Ind. Acad. Sci.*, 1937, **7 A**, 196.
3. Birckwedde, F. G., and Peters, M. F. *Phys. Rev.*, 1929, **33**, 116.
4. Landsberg, G., and Mandelstamm, L. *Z. f. Phys.*, 1930, **60**, 364.
5. Ornstein, L. S., and Went, J. J. *Physica*, 1935, **2**, 503.

PHYSICO-CHEMICAL STUDIES WITH AQUEOUS FLUORIDE SOLUTIONS

Part I. The Decomposition and Discharge Potentials of Some Fluorides in Aqueous Solution

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It is well known that fluorides of metals differ noticeably from the corresponding other halides and present several points of considerable interest. A survey of the literature on the subject reveals that in regard to the physico-chemical properties of fluorides there is still, in general, a paucity of information. A systematic detailed investigation of the important properties of aqueous fluoride solutions has been undertaken by the author, and the present paper contains the results of a study of the decomposition potentials and the discharge potentials of some aqueous fluoride solutions at various concentrations with polished platinum electrodes at 25° C. Quite recently, Crockford and Loftin[1] have studied the behaviour of aqueous solutions of hydrofluoric acid and certain alkali fluorides on electrolysis at 0° and 25° C. with stepwise increase of applied voltage across rotating, smooth platinum electrodes. From the results obtained they came to the conclusion that electrolytes of the type of hydrofluoric acid and the alkali fluorides have no true decomposition potential in aqueous solution. It appeared to the author that a more detailed study of the problem might lead to a better understanding of it; the present investigation was accordingly undertaken.

Experimental

Preparation of Materials.—All apparatus such as containing vessels, beakers, funnels, pipettes, measuring flasks, titration flasks, stirrers, etc., that were to come in contact with hydrofluoric acid or a fluoride solution, were coated with paraffin wax and calibrated thereafter whenever necessary. A platinum basin was used for the preparation of the fluorides.

All the fluorides were prepared in a pure condition in this laboratory except ammonium fluoride, potassium hydrogen fluoride and hydrofluoric acid which were Merck's guaranteed reagents. The methods given in Mellor's

A Comprehensive Treatise on Inorganic and Theoretical Chemistry were followed.

The alkali fluorides (LiF, NaF, KF) were prepared from the corresponding acid fluorides by thermal decomposition (Guntz's method[9]). Lithium hydrogen fluoride and sodium hydrogen fluoride were prepared, starting from lithium carbonate and sodium hydroxide respectively, and treating them with hydrofluoric acid.

Cadmium fluoride was obtained by the action of hydrofluoric acid in slight excess on cadmium carbonate. The mass was evaporated to dryness and then dried completely in an air-oven.

Antimony fluoride was prepared by dissolving the trioxide in excess of hydrofluoric acid and evaporating the solution very slowly on a water-bath till crystals began to appear. On cooling, large colourless plates separated out (Berzelius, Guntz, Flückiger[10]). These were removed and dried between folds of filter-paper, weighed and dissolved in a known volume of water. Further drying was found unnecessary; in fact, the crystals were found to decompose on drying over sulphuric acid and then did not dissolve completely in water. Analysis corresponds with the composition SbF_3.

Silver fluoride was prepared by dissolving freshly precipitated silver carbonate in hydrofluoric acid and filtering off any residue. The resulting clear filtrate was found to give a brown or black, sparingly soluble, hard mass on being evaporated to dryness. Hence the clear colourless solution itself was diluted as required and kept in darkness in bottles lined from inside with paraffin wax and protected from the action of light by covering from outside with opaque, black, glazed paper. The operations in the preparation of silver fluoride were carried out in darkness. During a determination also, the solution was kept screened from light. Analysis showed the presence of free hydrofluoric acid to the extent of one mole of the acid for every two moles of silver fluoride. The solutions of silver fluoride were found to decompose on keeping, so the analysis and measurements were made soon after the solutions were prepared.

The fluoride solutions, except that of silver fluoride, were prepared by dissolving weighed quantities of the fluorides in the requisite amount of conductivity water; exact normalities were determined in all cases by titration with a 0·02 N solution of thorium nitrate using Willard and Winter's method[2] for the estimation of fluoride as modified by Armstrong.[3] The thorium nitrate solution was standardised against a 0·02 N solution of Merck's *pro-analysi* hydrofluoric acid; the latter was prepared by dilution from a more concentrated solution, which was standardised against a decinormal solution

of potassium hydroxide using phenolphthalein as indicator. The normality of the diluted acid solution was checked by iodometric method.

Experimental Procedure and Other Details.—Decomposition potentials have, in the past, been measured in two ways: one, the direct method, and the other the commutator method. There has been much controversy regarding the correctness of the one or the other method, as the results obtained by the two methods are not in very close agreement. It has been definitely shown by Ferguson and Van Zyl,[4] and by Knobel,[5] however, that the direct method is the more correct method ; this method has been employed in the present investigation.

An electrically controlled water thermostat regulated at $25° \pm 0{\cdot}1°$ C. was used. The electrolytic cell consisted of a 400 c.c. beaker. The electrodes consisted of two polished platinum foils, each 3 sq. cm. in area, and kept 5 cm. apart. The electrode stems were sealed into ends of glass tubes filled with mercury for making electrical contact. The glass tubes carrying the electrodes were passed through holes in a thick wooden disc and sealed in position with paraffin wax. Another hole in the disc carried a thermometer for recording the temperature of the fluoride solution. The disc was also pierced for accommodating a stirrer between the electrodes to keep the electrolyte rapidly stirred in order to eliminate concentration polarisation and to prevent the accumulation of gas bubbles on the electrode surface. To attain this end the previous workers[1] rotated the electrodes themselves.

A gradually increasing potential from two storage batteries connected in series was applied to the electrolytic cell until the decomposition point was well nigh passed. At each stage the potential difference set up between the electrodes was measured with an accurately calibrated potentiometer, and the current flowing was measured by means of a milliammeter in conjunction with an accurately calibrated demonstration galvanometer. Variations in current of the order of 0·01 milliamp. or even less could be easily detected, while the potentiometer could easily detect a variation in potential of 0·25 millivolt.

After each run, the electrodes were cleaned in moderately concentrated nitric acid and washed thoroughly with conductivity water. Each of the electrodes was used alternately as cathode and anode in order to compensate for any difference between them ; no difference, however, was detected. Usually three to four runs were made for each salt at each concentration, and at least one check run was always made.

The same procedure was adopted in determining the discharge potentials; the standard half-cell used in these measurements was decinormal calomel electrode. In the case of silver fluoride, a salt bridge consisting of saturated

potassium nitrate was used. In other cases the tip of the calomel electrode was kept in contact with the electrode to be measured.

Typical current-voltage curves are shown in Fig. 1. Only a few points have been shown on each curve, but the curves were actually drawn through a large number of points. The curve for sodium fluoride is typical of the alkali fluorides and ammonium fluoride. Curves for LiF, NaF, KF, NH_4F, KHF_2, SbF_3 have two breaks each, while those for HF, AgF and CdF_2 have only one break each. The first break for KHF_2 is not well marked.

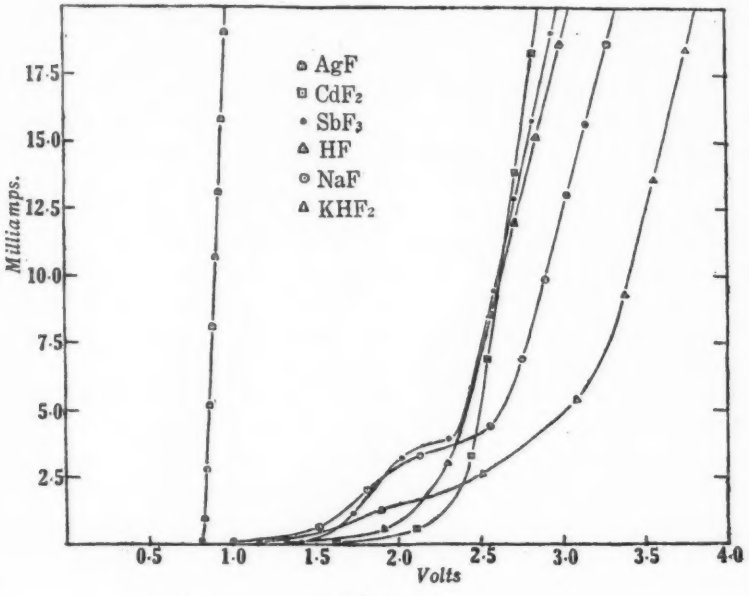

FIG. 1

Current-voltage curves for aqueous solutions of fluorides

Evaluation of Decomposition Potential.—In cases where the current-voltage curve exhibits a sharp break, the corresponding potential is quite definite and can be accurately determined. But if the break is not sharp, as is always the case when gaseous products are formed, or where secondary electrode reactions prevail, the value of the corresponding potential is not so definite and depends upon the procedure adopted in determining it. One method is to produce the straight parts of the curve until they intersect; a second procedure is to extrapolate the part of the curve for high current densities back to zero current density ; again, a third method is to plot the

logarithm of current density against voltage, and to take the potential corresponding with the intersection of the resulting straight lines as the decomposition potential. All these methods, however, are entirely arbitrary. A change in the scale of plotting a given set of data also changes to some extent the apparent position of the decomposition potential from round curves. The determination of the decomposition potential from round curves cannot, therefore, be made with the same degree of accuracy and certainty as from curves having sharp breaks.

In the present investigation, in determining the potential corresponding to a break in the current-potential curve, the method of producing the straight parts of the curve till they intersect has been followed ; because, in the first place, this makes the present data comparable with that of the previous workers[1]; secondly, other methods were found to be unreliable in some particular cases.

Results

Groening and Cady[6] have made a distinction between static decomposition voltage and dynamic decomposition voltage. The former refers to the minimum voltage at which electrolysis just begins, and the electrode processes are practically reversible. The dynamic decomposition voltage is the lowest voltage at which, during electrolysis, the electrode processes are the same as they would be if electrolysis with considerable current density were taking place, and is thus equal to the static decomposition voltage *plus* the cathode and anode overvoltages. It is important to bear this distinction in mind in discussing data on current-voltage relationships.

The potentials for each of the breaks in the current-voltage curves for the fluorides studied are given in Table I, and correspond to dynamic decomposition voltages *plus* the IR drop across the electrodes.

The values for KCl and HCl have been given for comparison. Wherever two breaks occur the potential for the second break has been taken as the true decomposition potential for the fluoride solution concerned except in the case of antimony trifluoride for which the potential for the first break has been taken as the decomposition potential (*vide infra*).

The discharge potentials referred to hydrogen as zero are listed in Table II. In calculating these values the potential of the decinormal calomel electrode at 25° C. has been taken as $+0{\cdot}3376$ volt referred to hydrogen electrode as zero. The alkali fluorides and ammonium fluoride may be taken to behave similarly on electrolysis; hence the discharge potentials for ammonium fluoride alone have been determined.

TABLE I

Electrolyte	Normality	Potential in volts at 25° C.	
		First break	Second break
LiF	0·056	1·61	2·95
NaF	0·778		2·60
	0·389		2·65
	0·195	1·53 ± 0·02	2·69
	0·078		2·76
KF	0·835		2·72
	0·417		2·75
	0·209	1·50 ± 0·02	2·77
	0·083		2·80
NH_4F	0·794		2·65
	0·397		2·62
	0·199	1·62 ± 0·01	2·61
	0·080		2·61
KHF_2	1·923		3·23
	0·769	1·55 ± 0·05	3·04
	0·240		3·01
SbF_3	0·948	1·63	2·40
	0·456	1·70	2·51
	0·119	1·86	2·93
HF	2·350	2·20	
	1·175	2·22	
	0·540	2·20	
	0·250	2·20	
	0·121	2·24	
	0·047	2·26	
AgF	1·296	0·73	
(Contains free HF in the proportion 2 AgF–HF)	0·518	0·83	
	0·162	0·90	
CdF_2	0·420	2·39	
	0·240	2·37	
	0·120	2·38	
KCl	1·000	2·22	
HCl	1·000	1·31	

TABLE II

Discharge Potentials at 25° C.

(Hydrogen Electrode = Zero)

Electrolyte	Normality	Cathode potential		Anode potential
		First break	Second break	
NH_4F	0·794	+0·12	−0·50	1·74
KHF_2	1·923		−0·85	2·12
	0·769	−0·17	−0·93	2·09
	0·240		−1·02	2·00
SbF_3	0·948	+0·14	−0·17	2·08
	0·456	..	−0·20	2·03
	0·119	..	−0·22	2·00
AgF	1·296	+0·74		1·51
(Contains free HF in the proportion 2 AgF–HF)	0·518	+0·72		1·56
	0·162	+0·69		1·58
CdF_2	0·420	−0·44		1·92
	0·240	−0·45		1·91
	0·120	−0·46		1·90

Discussion

In cases where the current-voltage curve has two breaks, the corresponding current-cathode potential curve also exhibits two breaks; but the current-anode potential curve has only one break in every case. From this it is evident that the occurrence of two breaks is due to two different processes at the cathode.

In cases where the current-voltage curve shows more than one break the question arises as to which of these should be taken to correspond with the decomposition voltage. According to the widely accepted definition of decomposition voltage[7] as the minimum voltage required for continuous electrolysis (with unattackable electrodes), the potential for the first break ought to be taken as the decomposition potential in every case.

But in the case of the alkali fluorides and ammonium fluoride it appears that the potential for the first break cannot be regarded as the true decomposition potential for these fluoride solutions, because the first break, which occurs at about $1 \cdot 55 \pm 0 \cdot 05$ volts for each of the above fluorides at different concentrations, and which according to the previous workers[1] is independent

of temperature also, corresponds, without doubt, to the primary decomposition of water, *i.e.*, the discharge of H^+ and OH^- ions only at the electrodes. Moreover, there is no break in the current-anode potential curve corresponding with the first break in the current-voltage curve. Further, if the logarithmic method of plotting is used, the first break becomes indistinct and uncertain in every case, while the second break is still very pronounced. The potential for the second break varies with the nature of the metallic ion, and in general, with concentration of a given fluoride solution, but is independent of the rate of stirring provided it is rapid enough to eliminate concentration polarisation and to prevent accumulation of gas bubbles on the electrodes. The previous workers[1] have found that it varies with temperature also. On the basis of these observations the second break may be assumed to be due to the primary electrode process being the discharge of the metallic ions and the fluoride or complex anions existing in solution; and as the products of such a discharge process will readily disappear by reaction with water as soon as they are formed, the above assumption is quite in harmony with the fact that the net electrolytic change is the decomposition of water alone. The potential for the second break may, therefore, be taken as the true decomposition potential for aqueous solutions of the alkali fluorides and ammonium fluoride.

The previous workers[1] are of opinion that as the potential for the normal fluorine electrode is very much higher than the potential required for the decomposition of water, primary decomposition of a fluoride cannot occur in aqueous solution, and the only electrolytic reaction during the entire course of electrolysis is the primary decomposition of water alone, so that for electrolytes of the type of hydrofluoric acid and the alkali fluorides, no true decomposition potential exists in aqueous solution. Such a view, however, seems to be untenable; because in the first place, it fails to account for the occurrence of the second break. One possible explanation might have been that at the second break, either the hydrogen or the oxygen or both, evolved at the electrodes, are in the atomic or excited state. But the difference between the values of potentials for the first and second breaks is far too small to admit of such an explanation. Secondly, the objection against the primary electrode process being the discharge of the metallic ions and the fluoride or complex ions and on the basis of the high potential for the normal fluorine electrode appears to be groundless from analogy with the behaviour of other alkali salts on electrolysis. Le Blanc's values for the decomposition potentials of normal aqueous solutions of the alkali chlorides, bromides and iodides are given in Table III. Undoubtedly, the primary electrode process at these potentials is the discharge of the alkali metal ions and the halide ions. These

values are, however, much lower than those calculated on a theoretical basis from the normal electrode potentials of the different metallic and halogen ions as can be seen from the figures in Table III. The same is true for the alkali sulphates, nitrates, etc.

TABLE III

Decomposition Potential in Volts for Normal Solution

Salt	Le Blanc's experimental values	Theoretically calculated values
LiCl ..	1·86	4·32
NaCl ..	1·98	4·08
KCl ..	1·96	4·28
NaBr ..	1·58	3·79
KBr ..	1·61	3·99
NaI ..	1·12	3·26
KI ..	1·14	3·46

The difference is obviously due to quick secondary changes on electrode surfaces making themselves felt. A comparison of such figures would be of still less value in the case of fluoride solutions on account of the existence of different kinds of complex ions, the concentration and influence of which are at present not well understood. Evidently, as depolarisation occurs in the presence of complex ions, the salt ions present in fluoride solutions may certainly be discharged at potentials lower than the theoretical value for the elementary ions.

Antimony fluoride also gives two breaks, each of which, however, varies with concentration. When a potential lying between those for the first and second breaks is applied, oxygen is evolved at the anode, although the quantity evolved is very minute; but there is no evidence of gas evolution at the cathode even after continuing the electrolysis for 6 hours. The cathode was, however, fogged, and assumed a shining, brown or black appearance. This was found to be due to the formation of a very thin film of antimony on the cathode. On increasing the potential to that for the second break, oxygen was still evolved at the anode, and antimony separated out in the form of small shining granules at the cathode. The current-cathode potential curve for antimony fluoride also gives two breaks which correspond to the two breaks in the current-voltage curve. The cathode discharge potential for the first break for 0·948 N solution of antimony fluoride (+0·14 volt, *cf.* Table II) corresponds approximately to the potential of the normal antimony electrode (+0·1 volt). The current-anode potential curve gives only one break which corresponds to the first break on the current-voltage curve.

From the above it appears that with antimony fluoride the potential for the first break may be taken as the decomposition potential. The occurrence of two breaks may be due to the separation of antimony in two different forms, and not to a change in the nature of the electrode processes.

Cadmium fluoride and silver fluoride also undergo true decomposition in aqueous solution, cadmium and silver being deposited at the cathode at potentials (*cf.* Table II) not considerably different from the normal electrode potentials for these metals (Cd, $-0{\cdot}40$ volt; Ag, $+0{\cdot}7995$ volt). Hence the decomposition potentials determined for these fluoride solutions are the true decomposition potentials. The behaviour of silver fluoride is, however, remarkable in that instead of a gas being evolved at the anode, as is the case with other fluoride solutions, a crystalline deep brown or black deposit is formed on the anode. This may be the reason why the anode discharge potential becomes more positive on dilution in the case of silver fluoride alone. This deposit was found to be almost insoluble in water, but it gave a deep brown solution with concentrated nitric acid. On the addition of a trace of potassium nitrite the solution at once turned colourless but remained very slightly turbid; the turbidity disappeared on heating. It is well known that a black crystalline deposit is formed on the anode when an aqueous solution of silver nitrate or silver sulphate is electrolysed between polished platinum electrodes. This black deposit is a peroxidised product. For details, *cf.* Mellor's book.[8] The nature of the product obtained with silver fluoride is being investigated in detail and will be communicated later. However, this product seems to be fundamentally similar to those obtained with silver nitrate and silver sulphate. A preliminary analysis shows the presence of about $80{\cdot}59\%$ of silver which, on the assumption that the product is a peroxide, corresponds most closely with the formula Ag_2O_3.

Reference has already been made to the earlier work by Crockford and Loftin[1] on the electrolysis of aqueous solutions of hydrofluoric acid and the alkali fluorides at 0° and 25° C., between smooth platinum electrodes. These workers also found two breaks in the current-voltage curve for the alkali fluorides. The first break for each fluoride solution had a value lying between $1{\cdot}62 \pm 0{\cdot}05$ volts at both the temperatures. The values for the second breaks at 25° C. are listed in Table IV and are the total bath potentials up to this point.

There is a marked discrepancy between the corresponding values of Tables I and IV. This discrepancy, however, on closer examination, seems to be only an apparent one. The previous workers[1] state that in making a determination, approximate curves were obtained, and then accurate data were

TABLE IV

(*After Crockford and Loftin*)

Electrolyte	Normality	Potential in volts for the second break at 25° C.
HF ..	0·108	1·62
LiF ..	0·045	2·47
KF ..	0·100	2·35
	1·000	2·23
NaF ..	0·100	2·32
	0·755	2·23

obtained by taking a large number of readings at the critical parts of the curves. By this means they have probably determined the potential at which the current just begins to rise abruptly—this being the critical point in the current-voltage curve; hence the values given in Table IV are, in all probability, the static decomposition voltages (*vide supra*) *plus* the IR drop across the electrodes; whereas the values given in Table I are the dynamic decomposition voltages *plus* the IR drop. Some ambiguity may, at first sight, arise in regard to the above interpretation of the previous workers' results on account of their statement that the potential up to the second break includes also the overvoltages of the hydrogen and oxygen discharge on smooth platinum in the respective solutions. It may be pointed out, however, that on the probable assumption of the primary electrode process at the second break being the discharge of the salt ions, the above statement is of no significance.

The author is indebted to the King Edward Memorial Society of the Central Provinces, Nagpur, for a research scholarship which enabled him to undertake this investigation, and to Dr. A. N. Kappanna, of the College of Science, Nagpur, for invaluable help and guidance.

Summary

The decomposition potentials of HF, LiF, NaF, KF, NH_4F, KHF_2, AgF, CdF_2 and SbF_3, and the cathode and anode discharge potentials of NH_4F, KHF_2, AgF, CdF_2 and SbF_3, in aqueous solution, have been determined at 25° C. at various concentrations using polished platinum electrodes. The current-voltage curves for LiF, NaF, KF, NH_4F and KHF_2 have an initial break at about $1{\cdot}55 \pm 0{\cdot}05$ volts for each concentration, and another break at a higher potential which varies with the nature of the metallic ion,

and also with the concentration of the fluoride solution. The curve for SbF_3 also has two breaks, each of which, however, varies with concentration. The curves for HF, CdF_2 and AgF have only one break each. Of the current-cathode potential and current-anode potential curves obtained, only the current-cathode potential curves for NH_4F, KHF_2 and SbF_3 have two breaks corresponding to the respective breaks in the decomposition current-voltage curves; the other curves have only one break each. These results have been discussed in detail and the inference is drawn that even alkali fluorides may have a true decomposition potential in aqueous solution.

REFERENCES

1. Crockford and Loftin .. *Trans. Amer. Electrochem. Soc.*, 1934, **66**, 239.
2. Willard and Winter .. *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 7.
3. Armstrong .. *J. Amer. Chem. Soc.*, 1933, **55**, 1741.
4. Ferguson and Van Zyl .. *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 337.
5. Knobel .. *J. Amer. Chem. Soc.*, 1924, **46**, 2613.
6. Groening and Cady .. *J. Phys. Chem.*, 1926, **30**, 1597.
7. Blum and Vinal .. *Trans. Amer. Electrochem. Soc.*, 1934, **66**, 359.
8. Mellor .. *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, **3**, 482–84.
9. Mellor .. *Ibid.*, 1922, **2**, 512.
10. Mellor .. *Ibid.*, 1929, **9**, 463.

FIXATION OF AROMATIC DOUBLE BONDS

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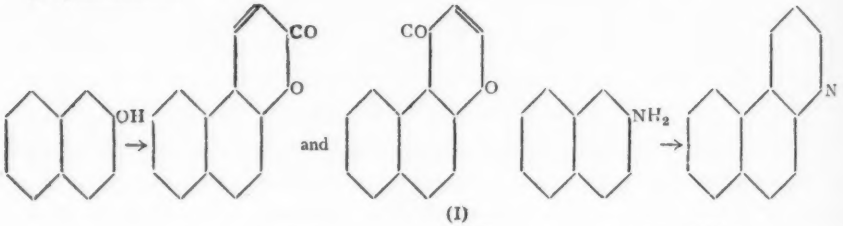
Introduction

The essential feature of the theory of Kekule relating to the structure of the benzene ring is the existence of oscillating double bonds. Consequently they should have no fixed positions. Based upon this idea the properties and reactions of the compounds of the aromatic series were considered to be satisfactorily explained. When therefore the possibility of the fixation of these bonds in certain favoured positions was announced, it attracted considerable attention and a great deal of work has been done with a veiw to get clear information of the behaviour of aromatic ring systems.

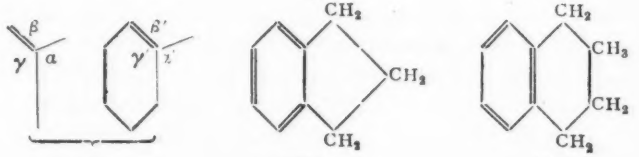
Work carried out towards the end of the last century and the beginning of this century with reference to derivatives of naphthalene and anthracene indicated the existence of certain select active positions. Fresh rings when formed tended to be of the angular type and not of the linear, as for instance, β-naphthol and β-naphthylamine formed rings (α- and γ-pyrone and pyridine rings) involving the 2:1 positions and not the 2:3 as shown in (I). The same phenomenon was noticed in the case of β-substituted anthracenes and anthraquinones. A similar preferential activity was noticed in other reactions such as bromination, nitration, aldehyde formation, etc. But the first to develop a theory on the fixation of aromatic double bonds were Mills and Nixon and the phenomenon is sometimes called the Mills-Nixon effect. If in a doubly bound carbon atom the angle α between the two single bonds is the same as that between the valencies of the carbon atom in methane (109°·5) then the angles β and γ which the single bonds make with the plane of the double bond would be each equal to one half of (360° − 109°·5) or 125°·25; *i.e.*, β is equal to γ and is greater than α (*vide* II). In the benzene ring each internal angle is 120°, *i.e.*, γ' is 5° less than γ. If this reduction of 5° in the value of γ' brings about proportionate increases in the values of α' and β' then the difference between these latter (α' and β') will be slightly more than that between α and β. In other words, in the benzene nucleus constituted in accordance with the Kekule formula, the angle which each of the external valencies makes with the intranuclear single bond on

the one side of it is less than that which it makes with the plane of the double bond on the other side, these being roughly in the ratio of 109° : 125°.

On this hypothesis Mills and Nixon argued that the stable form of a compound in which the benzene ring is fused with a 5-atom ring (internal angle 108°) must be that in which the linking common to the two rings consists of a single bond since such a configuration produces little distortion in the normal directions of the external valencies. Similarly the stable form of a compound in which the benzene ring is fused with a 6-atom ring (internal angle 120°) must be that in which the common link is a double bond. Thus hydrindene should consist of an equilibrium mixture in which the form with the common single bond (III) preponderates, and tetralin of a mixture in which the form with the common double bond (IV) is preponderant.



(I)



(II) (III) (IV)

The effects of fixation are also brought about by fusion with other aromatic rings just as in naphthalene, anthracene, phenanthrene, etc. Carbocyclic rings having five atoms as in fluorene have a similar influence. Fusion with heterocyclic rings such as pyrones, furans, pyridine, etc., have also been studied. It is interesting to record that even such unstable rings as are found in chelate structures have a tendency to bring about fixation of the aromatic double bonds.

The Methods Employed

As already mentioned data obtained from the direction of closing up of fresh rings starting from hydroxy and amino compounds gave valuable indications. Substitution reactions such as bromination and nitration, entry of aldehyde and ketone groups and formation of quinones and acids

in the case of isomeric hydroxy and amino compounds were subsequently utilised. Ingenious methods involving reactivity of methyl groups and of halogens in alternative positions have been employed by Mills and collaborators. Probably the most sensitive of all these methods is the formation of azo-dyes by the action of certain reactive diazonium salts. This has been very largely used by Fieser who has been also responsible for introducing what is known as the blocking technique. If the orientation of the newly entrant groups is dependent upon the presence of a double bond between the carbon atom having a hydroxylic or amino substituent and its neighbour all these methods are capable of locating the position of the double bond. But, as has been frequently realised it is probably more correct to say that there is quantitative difference in reactivity rather than any essential difference in the quality of the neighbouring positions. Fieser's technique of blocking one of the alternative positions with an alkyl group comes in very useful in this connection, since competition between two alternative positions is eliminated (examples are given in detail in subsequent pages). Combining with the blocking technique the very sensitive method of azo-dye formation, he claimed to have in certain cases proved the existence of rigid fixation of aromatic double bonds (naphthalene, anthracene and hydrindene). Another satisfactory method that has been employed to a large extent by Baker in studying the effect of chelate rings was the migration of groups like allyl (Claisen) and acetyl (Fries) from oxygen to carbon. A combination of this procedure along with the blocking method has been employed by Rangaswami and Seshadri in the case of coumarins and chromones with very definite results.

The above chemical methods suffer from certain inherent difficulties since in a number of cases the treatment is not simple. Physical methods have the advantage that they do not disturb the condition of the molecules. The most valuable of these is the determination of dipole moments. The dissociation constants of isomeric acids and phenols have been employed in certain cases and so also the oxidation-reduction potentials of certain quinones. Evidences from Raman spectra, infra-red spectra, absorption and X-ray spectra have also been obtained in a few cases. The lowering of the melting point under water has found application in special cases where chelate ring structures are involved.

For an explanation of the terms 'reactive methyl' and 'reactive halogen' reference may be made to the article on the 'principle of vinylogy' by Fuson.[1] A reactive methyl group is generally identified by its capacity to react with aromatic aldehydes and less frequently with phthalic anhydride

or *p*-nitrosodimethylaniline while a reactive halogen is characterised by its replaceability with hydrogen on treatment with reducing agents like phosphorus and hydriodic acid or acid stannous chloride and with other groups on treatment with bases like alcoholic ammonia, aromatic amines, alkali hydroxides or piperidine.

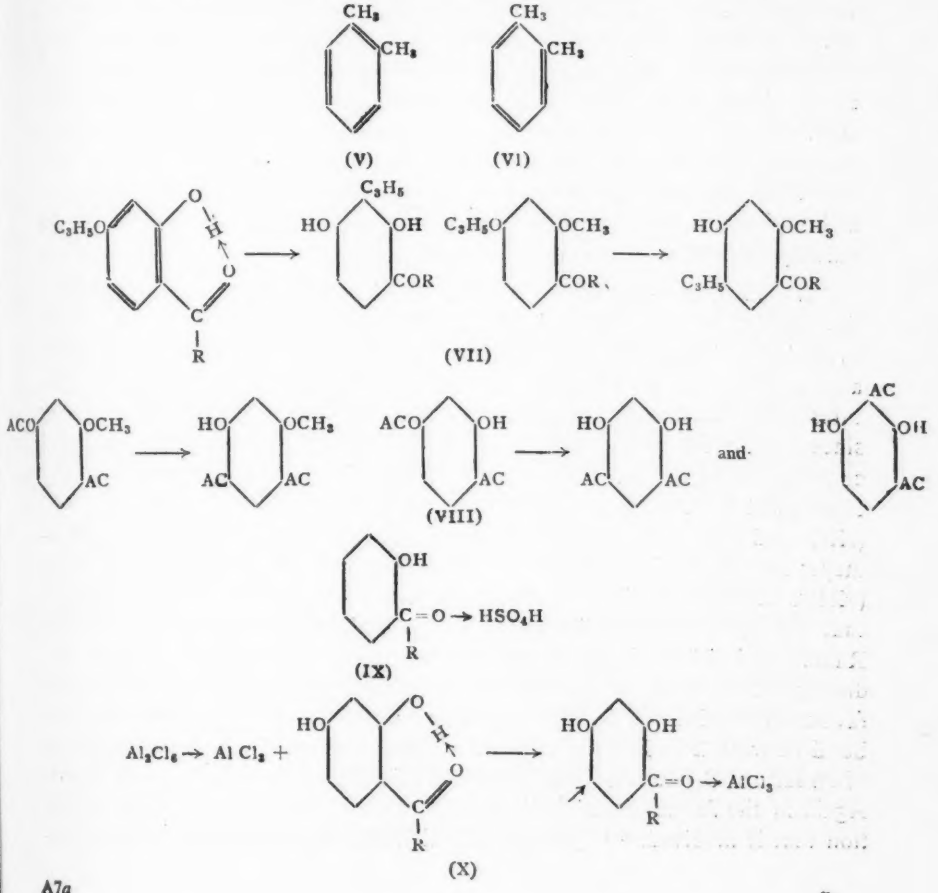
Details of the application of the above methods are given in the following pages where the examples of the important types are dealt with.

Benzene.—Considerable amount of work has been done in regard to the structure of this fundamental hydrocarbon molecule using delicate physical methods. All the results indicate that it has a plane symmetrical structure. Of the several chemical experiments made to determine the disposition of single and double bonds in benzene, that of Levine and Cole[2] deserves special mention here. As the result of ozonisation of *o*-xylene they obtained three products, *viz*., glyoxal, methyl-glyoxal and diacetyl. Neither form of the xylene can yield all the three oxidation products and hence the hydrocarbon should consist of an equilibrium mixture of the two Kekule forms (V) and (VI).

While this gives one side of the picture the work of Baker and others shows that fixation is possible under certain circumstances even in the simple benzene system. Baker and Lothian[3] found that 4-O-allylresacetophenone undergoes the Claisen transformation to produce mostly 3-allylresacetophenone though its methyl ether gives 5-allyl-2-O-methyl-resacetophenone under the same conditions (*vide* VII). Baker and Lothian explain these reactions by assuming that in the former case the existence of chelation between the adjacent hydroxyl and acetyl groups fixes one of the nuclear double bonds between the carbon atoms carrying these groups and the other two double bonds are in appropriate positions as shown in (VII). Hence the migration of the allyl group which involves the participation of a double bond is directed to the 3-position. When chelation is prevented as in the methyl ether then migration tends to produce a symmetrically substituted molecule.

Observations which support the above view have been made in connection with other types of reactions as well. Baker[4] found that though 2-methoxy-4-acetoxy-acetophenone gave 2-4 :-diacetyl-5-methoxy-phenol when subjected to the conditions of Fries migration, 4-O-acetylresacetophenone gave a mixture of 2 : 4- and 4 : 6-diacetylresorcinols under the same conditions owing to the operation of the forces of chelation in this case (*vide* VIII). Perkin[5] found that the methylation of β-resorcylic ester using methyl iodide and methyl alcoholic potash introduced a methyl group into the nuclear

position 3. Using ethyl iodide instead of methyl iodide Robinson and Shah[6] obtained similar ethylation in the same nuclear position. More recently Rangaswami and Seshadri[7] have found that under a similar treatment resacetophenone and ω-methoxyresacetophenone produce 3-C-methyl derivatives. Again Shah and others[8,9] have found that resorcylic ester and resacetophenone undergo the modified Gattermann reaction to give the 3-aldehydes. All these are in conformity with the hypothesis that chelation between the hydroxyl and the carbonyl in the *o*-position does involve a fixed nuclear carbon-carbon double bond. But at the same time the evidences accumulated by a number of workers go to show that this fixation is not very rigid and does not operate under all conditions. For example Baker *et al.* (*loc. cit.*) themselves conclude from the behaviour of resacetophenone



derivatives that 'fixation by chelation of the Kekule forms in *o*-hydroxy-acetophenones is not rigidly complete' though such fixation occurs 'to a considerable extent'. Similar conclusions can be arrived at from the nature of certain coumarin condensations as reported by Sethna *et al.*[10] These authors noted that whereas methyl β-resorcylate and aceto-acetic ester give methyl 4-methyl-5-hydroxycoumarin-6-carboxylate with aluminium chloride as the condensing agent, sulphuric acid produces 4-methyl-6-carbomethoxy-7-hydroxycoumarin; in the first case the γ-position of β-resorcylic ester is the reactive one whereas in the latter it is the free β-position.

The above irregularities are obviously due to the effect of reagents and temperature. Chelation is a special case of the wider phenomenon of hydrogen bond formation. From evidence accumulated in our laboratories chelate bonds seem to be some of the strongest of the type. Still they are not as strong as the ordinary covalent bonds and are possibly ruptured by such reagents as sulphuric acid which have the capacity of co-ordination to a high degree (IX). Regarding the influence of aluminium chloride somewhat contradictory results have been reported. Its behaviour probably varies considerably with the conditions and their effect on the changes represented in (X). It may also be mentioned here that chelation between a hydroxyl and a nitro group in the *o*-position does not seem to involve the participation of a nuclear double bond.

Naphthalene.—The structure of naphthalene is probably one of the most thoroughly investigated. A large number of methods have been employed to study the disposition of the nuclear bonds in one half of the molecule and also simultaneously in both the halves. Of the numerous canonical structures only the three represented in (XI), (XII) and (XIII) are important since they are the most stable valence bond structures and make the maximum contribution to the resonance energy of the naphthalene molecule. Among these three since (XII) and (XIII) are equivalent only structures (XI) and (XII) need be considered here. The symmetrical formula (XI) due to Erlenmeyer represents the molecule as being on the whole more aromatic than (XII) and hence would be the more plausible. Kohlrausch[11] has reported that the unsymmetrical formula for naphthalene is inconsistent with the Raman and infra-red spectra of the hydrocarbon though the data do not distinguish between the various symmetrical formulæ. Chemical evidence favouring the idea of a double bond between positions 1 and 2 and of a single bond between 2 and 3 is abundant. Thus β-naphthol couples with diazonium salts at C_1 whereas 1-methyl- and 1-allyl-2-naphthols do not couple.[12,13] Again in the formation of naphthapyrones from β-naphthol it is the 1-position that is involved.[14,15] β-Naphthol allyl ether rearranges to give 1-allyl-

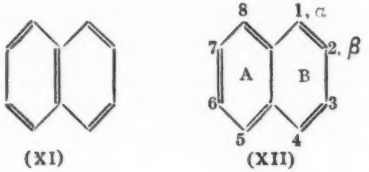
2-naphthol but 1-allyl-2-naphtholallyl ether does not rearrange (Claisen[13]). Again β-naphthylamine couples at C_1 to form azo-dyes and undergoes the Skraup reaction by ring closure involving position 1 (Marckwald[16]). The failure of 2:3-dihydroxynaphthalene to form a quinone (Marckward[17]) is definite proof that the HO·C·C·OH system here does not function as a single unit as it would do if the C atoms were connected by a double bond. Further evidence for the Erlenmeyer structure can be obtained from the reactivity (*i.e.*, elimination) of the halogen in chloro- and bromonitronaphthalenes (McLeish and Campbell[18]), bromo-aminonaphthalenes (Sandin and Evans[19]) and bromonaphthols (Franzen and Straube[20]). Again Hodgson and Elliot[21] found evidence for the symmetrical structure in the behaviour of halogeno-naphthylamines during acylation, nitration and hydrochloride formation while Bergmann and Hirschberg[22] concluded from the dissociation constants of *o*-chloronaphthoic acids that in naphthalene the single and double bonds have a fixed disposition as depicted by Erlenmeyer and do not undergo any rearrangement.

Strictly speaking all the above chemical evidence proves the disposition of bonds only in one part of the molecule. They do not necessarily indicate a symmetrical structure for the entire molecule and can be explained even on the structure (XII) if B is the nucleus carrying the substituents. Even the diazocoupling of 2:7-dihydroxynaphthalene at positions 1 and 8 (Ruggli and Courtin[23]) is not incompatible with the structure (XII) if it be assumed that substitution first occurs at C_1 and then following a rearrangement to the alternative unsymmetrical structure at C_8. Hence Fieser and Lothrop[24] studied the behaviour of 1:8-dialkyl-2:7-dihydroxynaphthalene (XIV) and 1:5-dialkyl-2:6-dihydroxynaphthalene (XV) and found that they do not couple and that their allyl ethers do not rearrange. This furnishes conclusive proof regarding the distribution of bonds in the entire molecule. They are arranged as in Erlenmeyer's representation and do not change under the above conditions.

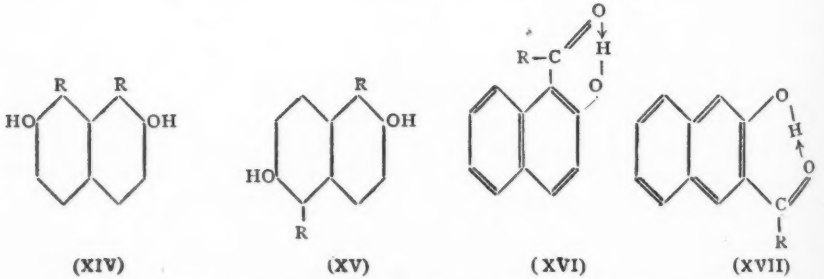
Thus far all the observations have gone to support the idea of the symmetrical structure (XI). The study of the dipole moments of some chlorinated naphthalenes by Hampson and Weissberger,[25] however, cast the first doubt on the above conclusion. According to them "each C–Cl bond in the chloronaphthalenes is directed as from the centre of the ring; if there is any fixation of single and double bonds in naphthalene it is not revealed in the direction of the substituents". Further evidence on the same lines was forthcoming from the work of Arnold and Sprung[26] who concluded from the values of the ionisation constants of isomeric *o*-hydroxy-naphthaldehydes that while a double bond was largely present between C_1 and C_2,

the presence of valence isomers with a double bond between C_2 and C_3 was also indicated. Also Baker and Carruthers[27] found a high degree of chelation not only in 2-acetyl-1-naphthol and 1-acetyl-2-naphthol (XVI) but also in 3-acetyl-2-naphthol (XVII). In the last compound the structure is definitely unsymmetrical with a double bond between C_2 and C_3. In the case of these hydroxy-aldehydes and ketones the change is probably brought about as the result of chelation. Purely chemical evidence for the presence of a double bond between C_2 and C_3 are the conversion of sodium β-naphthoxide to the 3-carboxylic acid (Schmitt and Burkard[28]) and the bromination of 1-bromo-*p*-toluenesulphon-2-naphthalide in the 3-position in pyridine solution (Bell[29]). The formation of 3-iodo-1-nitronaphthalene indirectly from 1-nitro-2-naphthyl-amine (Hodgson and Elliot[30]) is also another instance of the reactivity of the 3-positon in a 2-substituted naphthalene.

From the comprehensive data presented above regarding the behaviour of naphthalene derivatives it is clear that though the double bonds exhibit very marked tendency to be located as in the symmetrical Erlenmeyer formula the alternative positions are not altogether excluded. The characteristic properties of fixation are noticed in this ring system far more prominently than with the simpler benzene derivatives.



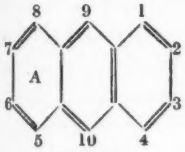
(XI) (XII) (XIII)



(XIV) (XV) (XVI) (XVII)

Anthracene.—Not much critical work has been done on polynuclear condensed ring systems. It was Armstrong who first put forward the view that in anthracene there is present at least one ring (A) which contains only two double bonds and which together with the ethylenic linkages extending into the central nucleus constitutes an *o*-quinonoid or dihydrobenzenoid

system of linkages. All the four stable valence bond structures (XVIII, XIX, XX and XXI) for anthracene are expressive of this idea. But (XVIII) and its counterpart (XX) are more plausible since these structures are on the whole more aromatic than (XIX) and its counterpart (XXI). With a view to test this, Fries *et al.*[31] studied the bromination of 2: 6-dihydroxy-anthracene and obtained the 1: 5-dibromo derivative; but though this result supports formula (XVIII) it is not incompatible with (XIX) if we assume that after substitution in one ring (A) the bonds undergo a rearrangement so as to confer on ring (C) the same structure as is initially present in (A) and *vice versa*. Hence Fieser and Lothrop[32] sought unequivocal evidence by studying the properties of 1: 5-dimethyl-2: 6-dihydroxy-anthracene (XXII). The failure of this compound to couple with diazotised amines definitely proved that in the anthracene structure the bonds are distributed as in (XVIII) and that the arrangement is immobile.



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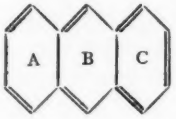
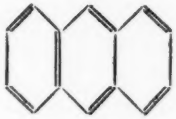
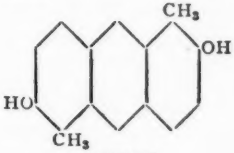


(XIX)


(XX)

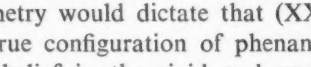
(XXI)



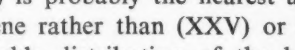
(XXII)

Phenanthrene.—Five stable valence bond structures are possible for phenanthrene as in (XXIII–XXVII) of which (XXV) and (XXVI) are equivalent. Mere inspection reveals that all the three rings tend to approach the ideal aromatic condition only according to the second representation (XXIV). The logical consequence would be that this structure would make a greater contribution to the resonance energy of the hydrocarbon than the others and the reactions and other behaviour of phenanthrene would be more in accord with it than with any of the other structures. Critical evidence which can throw light on this problem is neither exhaustive nor even adequate. The great ease with which the 9: 10 quinones are formed from phenanthrene and its derivatives indicates the presence of a double bond between these positions and thus definitely eliminates formula (XXVII). Smith[33] observed that 3-phenanthrol-4-aldehyde did not couple with diazotised amines simulating the behaviour of 1-methyl-2-naphthol; the evidence

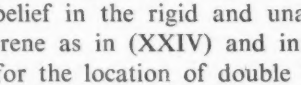
in this case is complicated by the existence of chelation as shown in (XXVIII). Recently Fieser, Young and Newman[34] have found that the allyl ethers of 2- and 3-phenanthrols undergo the Claisen transformation smoothly but the transformation products (obviously 1-allyl-2-phenanthrol and 4-allyl-3-phenanthrol) do not couple with diazotised amines and the allyl ether of the former does not again rearrange on heating. These evidences show that in phenanthrene the bonds are located as in (XXIV) or (XXV) [in the latter case if the substituents mentioned above are attached to ring (A) and not to ring (B)] and that structure (XXIII) is incompatible with these reactions. Though the behaviour of phenanthrene derivatives containing substituents in both the end nuclei does not seem to have been recorded, considerations of symmetry would dictate that (XXIV) is probably the nearest approach to the true configuration of phenanthrene rather than (XXV) or (XXVI). In fact belief in the rigid and unalterable distribution of the bonds of phenanthrene as in (XXIV) and in the infallibility of the diazo-coupling method for the location of double bonds has become so strong that this procedure has been employed by Fieser *et al.*[34] to assign the constitution of 2-retinol (XXIX) to the compound previously known as A-retinol. This compound had been prepared by Komppa and Wahlforss[35] and the chief argument in support of the constitution assigned by Fieser *et al.* was its inability to couple with diazotised amines.



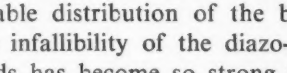
(XXIII)



(XXIV)

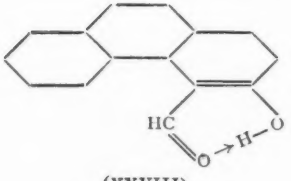


(XXV)

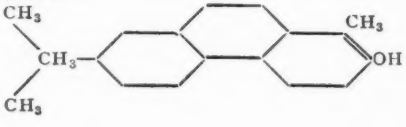


(XXVI)

(XXVII)



(XXVIII)

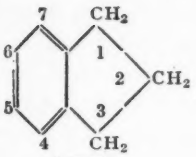


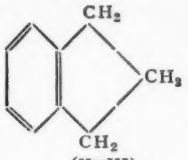
(XXIX)

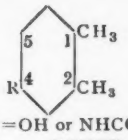
Hydrindene.—The earlier evidence on hydrindene seemed to favour the idea that it has a rigidly fixed bond structure with a single bond common to the two rings but more recently this has not been found to hold good in all cases of hydrindene derivatives. From theoretical considerations Mills and Nixon[36] concluded that in hydrindene the form with a common single bond (XXX) should be the more favoured structure and in support of this they showed that in 5-hydroxyhydrindene and 5-acetamidohydrindene it is the 6th position that is reactive to the almost complete exclusion of the 4th. Similar results had been obtained even as early as 1926 by Borsche and Bodenstein.[37] They found that 5-acetamidohydrindene gave the 6-nitro and 6-bromo derivatives on nitration and bromination respectively. These evidences, however, lose much of their significance when the behaviour of 4-hydroxy-1 : 2-dimethylbenzene and 4-acetamido-1 : 2-dimethylbenzene (XXXII) is considered. These compounds are reactive only in position 5[38,36] so that even in the 5-substituted hydrindene derivatives mentioned above the mere chemical effect of the methylene groups may be enough to explain adequately the formation of 6-substituted hydrindenes without any help from steric effects consequent on the fusion of the benzene ring with the 5-atom ring. Unambiguous evidence was therefore sought in the value of the dipole moment of 5 : 6-dibromohydrindene by Sidgwick and Springall.[39] They found for the Br·C·C·Br system of this compound a smaller value of the dipole moment than for the same system in *o*-dibromobenzene or in dibromo-*o*-xylene, thus proving definitely that there is no free resonance in hydrindene and that the rings have a common single bond. The same conclusion was arrived at by the application of the rigid chemical method developed by Fieser.[40] 6-Hydroxy-4 : 7-dimethylhydrindene (XXXIII) gave azo-dyes with diazotised amines but not 6-hydroxy-5-methylhydrindene (XXXIV). On the other hand pseudocuminol (XXXV) was able to couple with diazonium salts. Since chemically (XXXIV) and (XXXV) are similar the difference in the coupling capacity of the two compounds should be attributed to stereochemical effects. Obviously, owing to the fusion of the benzene ring with the polymethylene ring in (XXXIV), the $C_6 \cdot C_7$ link cannot behave like a double bond; in other words, the bonds of hydrindene are arranged as in (XXX) and this arrangement is unalterable. Further support to this conclusion was afforded by the results obtained by Arnold and Evans.[41] By the ozonisation of hydrindene followed by catalytic hydrogenolysis of the ozonide they obtained glyoxal and succinic acid (obviously from cyclopentane-1 : 2-dione). This indicates that hydrindene exists mostly as (XXX). The alternative structure (XXXI) would have given glyoxal and α-α'-diketopimelic aldehyde or its oxidation products, none of which were detected in the final mixture.

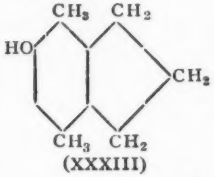
Results not entirely supporting the rigid structure given above were first obtained by McLeish and Campbell.[18] Besides finding that the bromine atom in 6-bromo-5-nitrohydrindene was highly reactive as mentioned above they noticed that the 4-bromo isomer also exhibited a feeble reactivity indicating a common double bond between the two rings (type XXXI). This was subsequently confirmed by Sandin and Evans[19] who, working mainly with 5-amino-hydrindenes with bromine atoms in the *o*-positions, found both the 6- and 4-bromine atoms reactive though to varying degrees. These authors however added that any inference that might be drawn was in favour of (XXX) being the favoured structure. A similar conclusion was drawn by Arnold and Zaugg[42] who found a higher oxidation-reduction potential for 4:7-hydrindenequinone (XXXVI) than for *o*-xyloquinone (XXXVII). This was attributed by these authors to a " positive Mills-Nixon type of partial double bond stabilisation " though the reasons for the use of the term ' partial ' are not clear. More definite evidence pointing to structure (XXXI) for hydrindene was furnished by the experiments of Fieser and Lothrop[43] who found that 5-hydroxy-6-methylhydrindene could form azo-dyes under certain carefully controlled conditions. A quantitative study of the diazo-coupling reaction led the latter author[44] to the conclusion that hydrindene derivatives were inferior to β-naphthol in coupling capacity and more comparable to 2:4-dimethylphenol. The smooth Claisen rearrangement of 5-allyloxyhydrindene when the 4- and 6-positions were separately blocked by methyl groups also lent support to the conclusion that the bond fixation in hydrindene derivatives is not very rigid.[44] The formation of 4:6-dibromo-5-amino-hydrindene by direct bromination of 5-aminohydrindene (Borsche and Bodenstein[37]) and the comparative values of the dissociation constants of 5-hydroxy-6-nitrohydrindene and of 2-nitrophenols (Arnold and Evans[45]) also show non-stabilization of double bonds as a result of ring fusion. Again from a study of the depression in melting point on wetting Baker[46] found that both 5-acetyl-6-hydroxy- and 5-acetyl-4-hydroxy-hydrindenes are chelated though to varying degrees. These compounds can exhibit chelation only if a single and a double bond respectively can be brought into being in common between the two rings in accordance with structures (XXX) and (XXXI) thereby enabling the chelate ring to possess a double bond. It may therefore be concluded that in hydrindene the structure with a common single bond is the more favoured though the other alternative is not excluded.

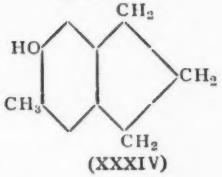
Tetralin.—According to the theoretical considerations developed by Mills and Nixon[36] tetralin should have a predominant structure in which a double bond is common to the two rings (XXXVIII). In support of their

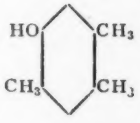

(XXX)

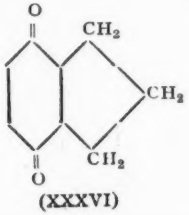

(XXXI)

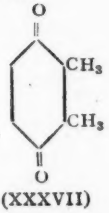

R=OH or NHCOCH$_3$
(XXXII)


(XXXIII)


(XXXIV)


(XXXV)

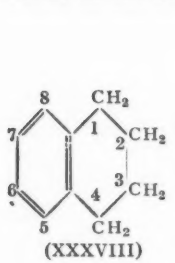

(XXXVI)


(XXXVII)

conclusion these authors quoted the previous findings of Schroeter[47] and of Smith[48] that 6-hydroxy- and 6-acetamidotetralin gave 5-substituted compounds in bromination and diazo-coupling experiments. Another evidence favouring this idea is the presence of a positive bromine atom in 5-bromo-6-aminotetralin (Sandin and Evans[19]) and in 5-bromo-6-hydroxy-7-aminotetralin (Schroeter[47]). This method however does not seem to be altogether satisfactory and consistent, since McLeish and Campbell[18] found proof for the alternative conclusion (common single bond, type XXXIX) in the behaviour of 6-bromo-5-nitrotetralin (unreactive) and 6-bromo-7-nitrotetralin (reactive). A result which is in conformity with the latter observation is the formation of 6-hydroxy-7-nitrotetralin from 6-hydroxy-tetralin (Thomas and Kross[49]). Thus tetralin seems to be capable of reacting in the alternative structural form (XXXIX) with equal facility.

That tetralin is really to be considered as made up of a mixture represented by the two structures was evident from the work of V. Braun and Grüber[50] who subjected 6-amino-tetralin to the Skraup reaction and obtained a mixture of the linear and angular varieties of the tricyclic compound (XL and XLI). The more subtle methods of investigation are also largely in favour of the idea that in tetralin there is no fixation of the double bonds and that there is resonance in the purely aromatic sense. Thus, Sidgwick and Springall[39] found that the Br·C·C·Br system in 6:7-dibromotetralin

had a value for the dipole moment equal to that in *o*-dibromobenzene and dibromo-*o*-xylene. Fieser and Lothrop[40] found that both 7-hydroxy-5: 8-dimethyltetralin (XLII) and 7-hydroxy-6-methyltetralin (XLIII) could couple with diazotised amines, while in quantitative experiments using the method of diazo-coupling tetralin derivatives were less reactive than β-naphthol and more akin to 2: 4-dimethyl-phenol (Lothrop[44]). Further Arnold and co-workers found 6-hydroxy-7-nitrotetralin and *o*-nitrophenols to have the same value for the dissociation constant[45] and 1,- 2,- 3,- 4- tetrahydronaphtho-5: 8-quinone (XLIV) and *o*-xyloquinone (XXXVII) to have nearly equal oxidation-reduction potentials[42] showing non-stabilisation of the double bonds in the tetralin system.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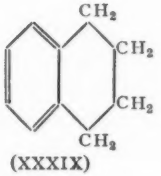
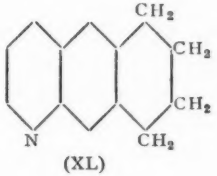
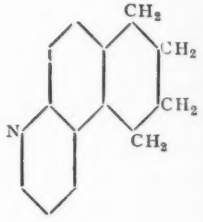
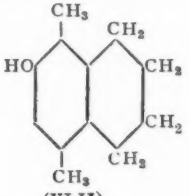
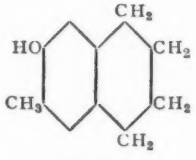
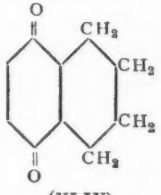

(XXXIX)


(XL)


(XLI)


(XLII)


(XLIII)

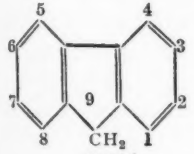

(XLIV)

Fluorene.—There are four important structures that can be formulated for fluorene. Of these the symmetrical ones (XLV) and (XLVI) would be the more plausible though the unsymmetrical ones (LXVII) and (LXVIII) cannot be altogether ignored in the absence of positive evidence in favour of such elimination. (XLV) represents the fluorene molecule as essentially derived from cyclopentadiene while (XLVI) looks more like a cyclopentane compound. Both of them contain an unbroken chain of conjugated double bonds and would have considerable stability.

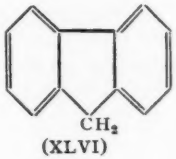
On the basis of refractivity studies Auwers *et al.*[51,52] concluded that the aromatic rings in fluorene must be classed as similar to naphthalene and anthracene at least qualitatively. From nitration experiments Ananthakrishnan and Hughes[53] obtained evidence for considering fluorene as dibenzocyclopentadiene. Subsequently Hughes, LeFevre and LeFevre[54] concluded

from studies of dipole moments that their data did not point to any specific configuration for fluorene whose structures may be flat degenerate forms between (XLV) and (XLVI).

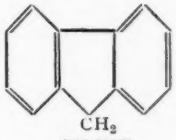
On the chemical side the evidence which is incomplete, inasmuch as it refers to only one of the benzene rings and not simultaneously to both, does not point to any rigid structure represented by either (XLV) or (XLVI). Thus γ-2-fluorene-butyric acid and *o*-2-fluorenebenzoic acid close up rings in such a way that the 3-position is involved.[55,56] These point to structure (XLVI) for fluorene. On the other hand 2-acetoxyfluorene and 2-acetoxyfluorenone undergo the Fries migration to give 1-acetyl-2-hydroxy compounds[57] thus pointing to structure (XLV). However, a great many fluorene derivatives behave as though there is no fixation of the double bonds in any position. Thus, Lothrop[58] found that 2-allyloxyfluorene underwent the Claisen transformation to give a mixture of isomers supposed to be the 1- and 3-allyl-2-hydroxyfluorenes; both 1 : 2-dimethyl-3-hydroxyfluorene (XLIX) and 1 : 4-dimethyl-3-hydroxyfluorene (L) coupled with diazotised amines and their allyl ethers smoothly underwent the Claisen transformation thus showing that either of the *o*-positions of 3-hydroxyfluorene can behave as a reactive centre in these reactions. Again 2-allyloxyfluorenone behaved just like 2-allyloxyfluorene in the Claisen transformation giving a mixture of isomeric products,[57] and the Kolbe's reaction with 2-hydroxyfluorene gave two isomeric acids (obviously the 1- and 3-carboxylic compounds).[59] Thus the balance of evidence seems to be in favour of the idea that in fluorene there is little fixation of the nuclear bonds just as in diphenyl.



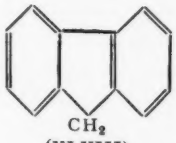
(XLV)



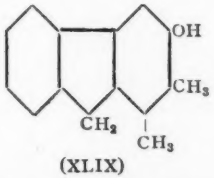
(XLVI)



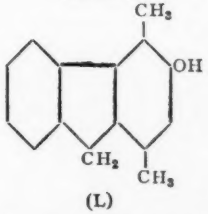
(XLVII)



(XLVIII)



(XLIX)



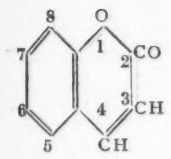
(L)

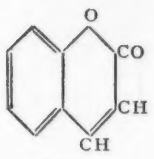
Coumarin and Chromone.—Though in coumarin itself substitution invariably takes place in the 6th position, in 7-hydroxycoumarins it is exclusively in the 8th position. When attempts are made to build up fresh rings

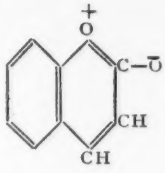
starting from 7-hydroxy-coumarins, it is the 8th position that is involved in the ring-formation. Thus employing 7-hydroxycoumarin and bromo-acetal Späth[60] obtained angelicin (LV). Rangaswami and Seshadri[61] similarly found that the Pechmann condensation between 7-hydroxycoumarins and malic acid or acetoacetic ester gave mostly the angular coumarino-α-pyrones (type LVI). Again attempts to introduce an aldehyde group into 7-hydroxy-coumarins gave the 8-aldehydes.[61,62] All these show that 7-hydroxy-coumarins react in the form (LI). The most reliable evidence for this structure, however, comes from the work of Baker and Lothian[3] who found that 7-allyloxy-4-methylcoumarin undergoes the Claisen transformation to give 7-hydroxy-8-allyl-4-methylcoumarin thus proving conclusively that there exists a double bond between the 7- and 8-positions.

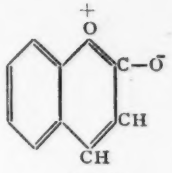
Evidence which does not fall into line with the above was first obtained by Limaye.[63] He found that when 4-methyl-7-acetoxycoumarin was subjected to Fries migration, the 8-acetyl-7-hydroxy compound which was the major product was accompanied by a small quantity of the 6-acetyl-isomer. The simultaneous formation of the angular coumarino-α-pyrone (LVI major product) and the linear isomer (LVII, minor product) from the Pechmann condensation using umbelliferone and malic acid (Rangaswami and Seshadri[61]) corroborates the above observation and shows the slight but significant reactivity of the 6th position in umbelliferone. The last-mentioned authors have applied Fieser's technique to the coumarin ring system and obtained unequivocal evidence on the distribution of the single and double bonds.[64] They have found that 7-hydroxy-4:8-dimethylcoumarin (LVIII) couples with diazotised *p*-nitraniline and forms with mercuric acetate a mercury derivative which contains 2-acetoxy-mercuri groups replaceable by bromine atoms. The allyl ether and acetyl derivative also smoothly undergo the Claisen transformation and Fries migration respectively. All these reactions can be explained only on the assumption of a reactive 6-position which is possible only if the bonds can take up positions as depicted in (LII). Thus in coumarins while the normal structure corresponds to (LI) the other is not precluded.

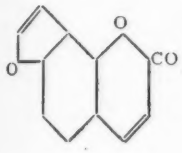
From a study of dipole moments Rau[65] concluded that coumarin exists in the excited state mainly as (LIII). Besides many others the alternative structure (LIV) (not mentioned by this author) is also possible in which the situation in the lactonic part is the same. A comparison of the two forms clearly shows that on the whole (LIII) represents a more aromatic structure than (LIV) and will tend to be the more important of the two forms in entire agreement with results deduced from chemical reactivity.

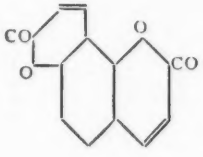

(LI)

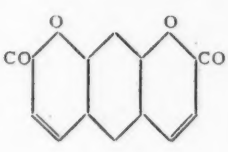

(LII)

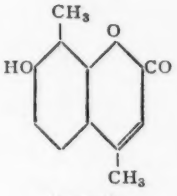

(LIII)


(LIV)


(LV)

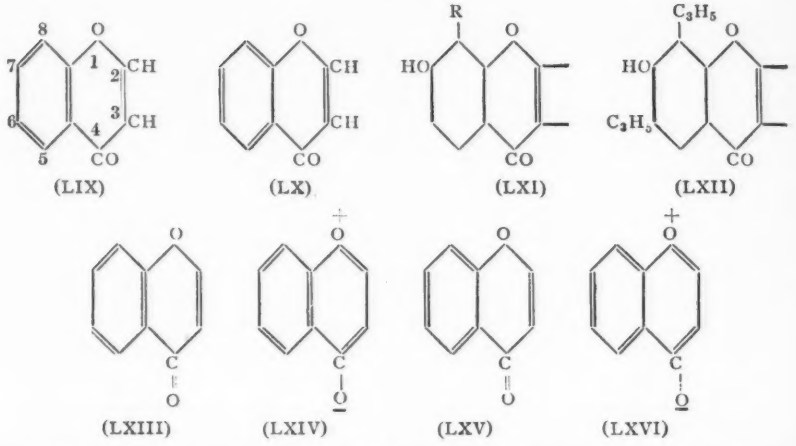

(LVI)


(LVII)


(LVIII)

The theoretical considerations of the structure of chromones and flavones (benzo-γ-pyrones) and the experimental study follow on lines closely similar to those applied to the coumarins (benzo-α-pyrones). The great reactivity of the 8th position in 7-hydroxy-chromones is evident from the formation of the 8-aldehyde from 7-hydroxy-3-methoxyflavone by the action of formylating agents (Rangaswami and Seshadri[66]). Again it is the 8th position that is involved in the Fries migration of 7-acetoxy-2-methylchromone (Wittig, *et al.*[67]) or its 3-acetyl derivative (Baker[68]) and in the Claisen transformation of the allyl ethers of 7-hydroxyflavone and 7-hydroxy-2-methyl-3-methoxychromone (Rangaswami and Seshadri[69]). These suggest a fixation of the double bonds as in (LIX). But the 8-allyl-7-hydroxy-compounds (LXI, R = allyl) obtained from the above Claisen transformations give allyl ethers which are capable of undergoing further Claisen rearrangement to give rise to the 6 : 8-diallyl-7-hydroxy-chromones and flavones (LXII).[69] This indicates that the nuclear bonds are capable of redistribution as in type (LX). Further support for this conclusion is afforded by the capacity of 8-methyl-7-hydroxyflavone and its 3-methoxy derivative (LXI, R = methyl) and of 8-allyl-7-hydroxyflavone and 8-allyl-7-hydroxy-2-methyl-3-methoxy chromone (LXI, R = allyl) to couple with diazotised *p*-nitraniline.[69] Thus the initial distribution and realignment of bonds in chromones are quite analogous to the case of coumarins.

A close examination of the formulæ (LXIII) to (LXVI) leads us to the same conclusion. (LXIV) represents the reactive or excited state of the molecule and it exhibits the maximum aromatic characteristics. (LXIII) corresponds to a *p*-quinone structure. In both these there eixsts a double



bond in common between the two rings and as a consequence the disposition of the other bonds in the benzene part is fixed. Structures (LXV) and (LXVI) represent other possibilities and have a single bond in common between the rings; but these are obviously less stable structures devoid of the maximum conjugation and their contribution to the behaviour of the molecule will be small. Though small it seems to be appreciable and definite as indicated by the experimental results recorded above.

The simultaneous reactivity of the 6- and 8-positions in the coumarins and chromones indicating the occurrence of the two alternative positions of the double bonds has been to some extent indicated by recent experiments. The formation of 6:8-disubstituted derivatives from 7-hydroxy-coumarin during mercuration, bromination and nitration using excess of the reagents does not really have much significance in this connection; it is possible to explain these reactions by assuming that first the attack is initiated at position 8 of the form (LI), the product subsequently changes into the form (LII) and then reacts with more of the reagent in position 6 to give the 6:8-disubstituted compounds, provided of course that the physical conditions are not adverse to the progress of this second stage of the reaction (*vide* Rao, Sastri and Seshadri[70]). On the other hand the simultaneous formation of the 8- and 6-acetyl-7-hydroxy compounds by the Fries migration of 7-acetoxy-4-methylcoumarin (Limaye[63]), and of the angular and linear coumarino-α-pyrones by the Pechmann condensation of 7-hydroxycoumarin and malic acid (LVI and LVII[61]), show that the 8- and 6-positions can be simultaneously reactive in these compounds. In support of this there is the evidence of Rangaswami and Seshadri[71] who have carried out quantitative diazo-

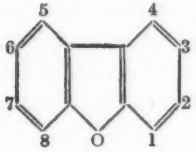
coupling experiments to study this question. Starting with 7-hydroxy-4-methylcoumarin and 7-hydroxy-2-methyl-3-methoxychromone and employing just one molecular proportion of diazonium salts they have obtained dyes whose compositions show that bis-azo-dye formation has taken place. This is not possible if the 6th position can become reactive only after the 8th has completely reacted, since in such a case the quantity of reagent used would have been completely used up by the 8th position. The fact that bis-azo-dyes were not formed in the case of all the coumarins and chromones studied under the influence of only one molecular proportion of the reagent does not invalidate the above conclusion regarding the simultaneous reactivity of the 6- and 8-positions. Obviously the substituent groups in these compounds are not altogether without an effect on the mobility of the nuclear bonds. This statement receives support from similar observations by the same authors in other types of reactions as well. Thus though umbelliferone and malic acid gave a mixture of coumarino-pyrones under the conditions of the Pechmann condensation only the angular compounds (reactive 8-position) were formed from 4-methyl-umbelliferone and malic acid or ethyl acetoacetate.[61]

Dibenzofuran

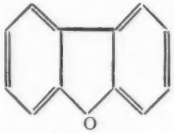
Four structures (LXVII to LXX) are important for dibenzofuran. LXIX and LXX which are equivalent among themselves are not likely to be as important as the other two inasmuch as they assume that the molecule is unsymmetrical. As between LXVII and LXVIII the former represents the hydrocarbon as a furan derivative, the latter as a dihydrofuran derivative. For maximum stability each component ring should have the maximum aromatic configuration and hence (LXVII) would represent the most important canonical structure. At the same time we find a high degree of conjugation even in (LXVIII) and hence the contribution of this form to the resonance energy would certainly come next in importance to that of (LXVII). Thus we seem to be having here a case similar to fluorene; the bonds can take up either of the alternative positions with equal ease.

A complete chemical investigation of this question would involve the study of substitution not only in one part of the molecule but simultaneously in both the end rings. Such definite proof, however, seems to be lacking. The available evidence, mostly the work of Gilman and his school, shows that there is no specially favoured disposition for the bonds, though it refers only to one of the benzene rings. The bromination and nitration of hydroxy-, methoxy- and acetamido-dibenzofurans[72] and the diazo-coupling of 2-hydroxy-, 3-hydroxy- and 4-hydroxy-dibenzofurans[73] give results some

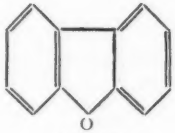
of which are in accord with formula (LXVII) while the rest are expressive of formula (LXVIII).



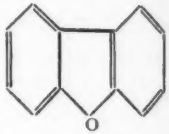
(LXVII)



(LXVIII)



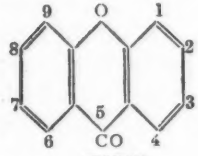
(LXIX)



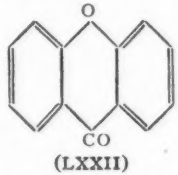
(LXX)

Xanthone and Xanthene

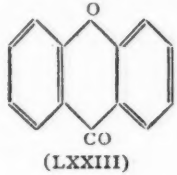
Four important structures (LXXI to LXXIV) are possible for xanthone of which, by analogy with chromones, the first would be expected to be the nearest approach to the true structure of the molecule. LeFevre[74] found that the dipole moments of 2:7-dibromo- and dinitroxanthones are in good agreement with the structure (LXXI) and further that the bonds are almost completely fixed as depicted in that formula. If fluorescein (LXXV) can be considered as a xanthene derivative then valuable information can be gathered regarding the distribution of bonds in this system from the reactivity of the dye as pointed out by Sandin, *et al.*[75] The data available regarding this compound have one welcome feature; derivatives containing substituents in both the benzene rings are easily available and are amenable to experimental study so that it is possible to get a complete picture of the entire molecule. Sandin and co-workers thus found that bromination of fluorescein and sulphone-fluorescein (LXXVI) produced 4:5-disubstituted



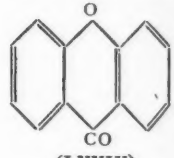
(LXXI)



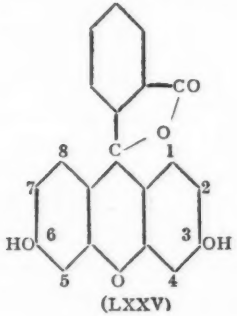
(LXXII)



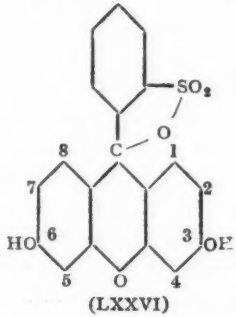
(LXXIII)



(LXXIV)



(LXXV)



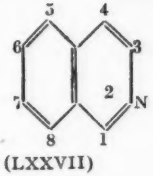
(LXXVI)

compounds (Orndorff, *et al.*[76]; Sandin *et al.*[75]) Further in tetrabromofluorescein and 4: 5-dibromo-2: 7-dichlorofluorescein, the 4 and 5 bromine atoms alone were found to be reactive (Sandin, *et al.*[75]). The dinitration of fluorescein again yielded the 4: 5-dinitro compounds (Hewitt, *et al.*[77]) and the formation of bis-azo-dyes from fluorescein involved the same two positions (Irgraffia[78]). All these suggest structures rigidly fixed as shown in (LXXI) for the xanthone system.

Quinoline and Isoquinoline

Chemical work relating to these systems was done as early as 1922. Three structures are possible for iso-quinoline (LXXVII to LXXIX). The work of Mills and Smith[79] showed that the methyl group in 1-methyl-iso-quinoline was reactive but not the methyl in 3-methyl-iso-quinoline. Similarly a chlorine atom in the 1-position was easily replaced by hydrogen on treatment with red phosphorus and hydriodic acid but not when it was present in the 3-position. These prove the existence of a double bond between positions 1 and 2 in isoquinoline and of another double bond between 3 and 4. Regarding the nature of the common link and of the bonds in the benzene part in iso-quinoline positive evidence is lacking, but it may probably be safe to assume that (LXXVII) is the closest approximation to the true structure of the molecule.

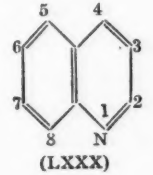
Mills and Smith[79] were of the opinion that in quinoline also the distribution of bonds should be just as in iso-quinoline, capable of representation by formula (LXXX). The theoretical structures are also of the same type as in iso-quinoline and their relative importance would be of approximately the same order of magnitude. Definite evidence was obtained by LeFevre and LeFevre[80] who concluded from the study of dipole moments of quinoline derivatives that the mobilities of the single and double bonds in quinoline derivatives are so diminished by ring fusion that the skeleton is best



(LXXVII)

(LXXVIII)

(LXXIX)



(LXXX)

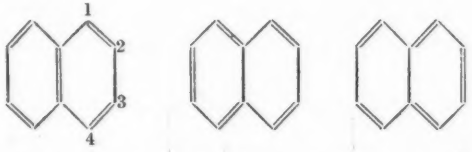
(LXXXI)

(LXXXII)

formulated as (LXXX) and this statement seems to hold good except when dynamic isomerism is rendered possible as in the case of 2-methylquinoline.

Discussion of Results and Conclusion

From the results presented in the foregoing pages it is clear that there has been a large amount of data of a chemical as well as physical nature relating to the question of the fixation of aromatic double bonds. It is possible that some of them might undergo modifications as a result of careful revision. This is due to the inherent difficulties of experimental technique in this line of work. Taking into consideration all factors there appears to be sufficient justification for concluding in favour of fixation of the double bonds. This fixation seems to be of varying degrees, being (1) very weak when chelate rings are the cause of fixation, (2) more prominent when heterocyclic rings are involved and (3) more or less rigid in polynuclear aromatic structures such as naphthalene, anthracene, etc. Apparently these statements may be objectionable from the physicist's point of view since it may be considered not to be in consonance with the discoveries that benzene and naphthalene are absolutely plane symmetrical structures. But the theory of resonance which has been developed and employed successfully during recent years seems to eliminate all difficulties. These ideas have been very adequately summed up by Pauling in his well-known recent book "*The Nature of the Chemical Bond*" (1st edition, pages 131–35). It has been shown that the stability and characteristic aromatic properties of benzene can be attributed to resonance of the molecule between two Kekule structures, each of the six bonds in the ring acquiring half a double bond character. For naphthalene three stable valence bond structures can be formulated as below:



As a consequence there is brought about considerable difference between the characteristics of the different bonds. Thus the bond between 1- and 2-positions has $\frac{2}{3}$ double bond character whereas the one between 2- and 3-positions has only $\frac{1}{3}$ double bond character with the result the former behaves very much like a double bond whereas the latter has very little double bond characteristics. This results in an enormous difference in reactivity giving rise to the well-known phenomenon which has been described as 'fixation'. In the case of anthracene and phenanthrene the differences

between the bonds are even greater owing to the existence of larger numbers of valence bond structures. No correct prediction has obviously been attempted of the nature of the bonds when substituents which can produce powerful electromeric effects such as the hydroxyl, amino, bromo and nitro are introduced in these aromatic structures. It may however be expected that the differences between the bonds will be further accentuated. Similar explanations can be given of the effect of heterocyclic rings and of chelate rings. But this fixation can never be absolutely rigid since the other bonds also have very small but still appreciable double bond characteristics. And when the more reactive positions are protected, the feebler reactivity of the others is exhibited especially with powerful reagents and under favourable conditions.

The above remarks hold good even in the case of what is known as the "Mills-Nixon effect" where saturated carbon rings, attached to two ortho positions of a benzene ring, make it react as though the double bonds were fixed in one or the other of the alternative positions.

REFERENCES

1. Fuson .. *Chem. Rev.*, 1935, **16**, 1.
2. Levine and Cole .. *J. Am. C. S.*, 1932, 338.
3. Baker and Lothian .. *J. C. S.*, 1935, 628; 1936, 275.
4. Baker .. *Ibid.*, 1934, 1684.
5. Perkin .. *Ibid.*, 1895, 990.
6. Robinson and Shah .. *Ibid.*, 1934, 1496.
7. Rangaswami and Seshadri *Proc. Ind. Acad. Sci.*, 1938, **8A**, 214.
8. Shah and Laiwalla .. *J. C. S.*, 1938, 1828.
9. ——— and Shah .. *Ibid.*, 1939, 132.
10. Sethna, Shah and Shah .. *Ibid.*, 1938, 228.
11. Kohlrausch .. *Ber.*, 1935, 893.
12. Fries and Hubner .. *Ibid.*, 1906, 435.
13. Claisen .. *Ibid.*, 1912, 3157.
14. Bacovescu .. *Ibid.*, 1910, 1280.
15. Dey and Lakshmi-narayanan *J. Indian C. S.*, 1932, 149. (See also Haworth, *J. C. S.*, 1932, 1125.)
16. Marckwald .. *Ber.*, 1890, 1015.
17. ——————— .. *Ann.*, 1893, 331; 1894, 1.
18. McLeish and Campbell .. *J. C. S.*, 1937, 1103.
19. Sandin and Evans .. *J. Am. C. S.*, 1939, 2916.
20. Franzen and Straube .. *J. Prakt. Chim.*, 1920, 58; 1922, 352.
21. Hodgson and Elliot .. *J. C. S.*, 1936, 1762.
22. Bergmann and Hirschberg *Ibid.*, 1936, 331.
23. Ruggli and Courtin .. *Helv. Chim. Acta.*, 1932, 110.

24. Fieser and Lothrop .. *J. Am. C. S.*, 1935, 1459.
25. Hampson and Weissberger *J. C. S.*, 1936, 393.
26. Arnold and Sprung .. *J. Am. C. S.*, 1938, 1163.
27. Baker and Carruthers .. *J. C. S.*, 1937, 479.
28. Schmitt and Burkard .. *Ber.*, 1887, 2702.
29. Bell .. .. *J.C.S.*, 1932, 2732. (See also Thompson, *Chem. Ind.*, 1933, 61.)
30. Hodgson and Elliot .. *Ibid.*, 1939, 345.
31. Fries, Walter and Schilling *Ann.* 1935, 248.
32. Fieser and Lothrop .. *J. Am. C. S.*, 1936, 749.
33. Smith .. .. *J. C. S.*, 1916, 568.
34. Fieser, Young and Newman *J. Am. C. S.*, 1931, 4120.
35. Komppa and Wahlforss .. *Ibid.*, 1930, 5009.
36. Mills and Nixon .. *J. C. S.*, 1930, 2510.
37. Borsche and Bodenstein .. *Ber.*, 1926, 1909.
38. Diepolder .. *Ibid.*, 1909, 2918.
39. Sidgwick and Springall .. *J. C. S.*, 1936, 1532.
40. Fieser and Lothrop .. *J. Am. C. S.*, 1936, 2050.
41. Arnold and Evans .. *Ibid.*, 1940, 2670.
42. Arnold and Zaugg .. *Ibid.*, 1941, 1317.
43. Fieser and Lothrop .. *Ibid.*, 1937, 945.
44. Lothrop .. *Ibid.*, 1940, 132.
45. Arnold and Evans .. *Ibid.*, 1940 556.
46. Baker .. *J. C. S.*, 1937, 476.
47. Schroeter .. .. *Ann.*, 1922, 83.
48. Smith .. .. *J. C. S.*, 1904, 730.
49. Thomas and Kross .. *Arch. Pharm.*, 1927, 336.
50. Braun and Grüber .. *Ber.*, 1922, 1710. (See also Lindner, *Etal, Monat-h*, 1924, 337.)
51. Auwers and Frühling .. *Ann.*, 1920, 220.
52. ——— and Krollpfeiffer .. *Ibid.*, 1923, 264.
53. Ananthakrishnan and Hughes *J. C. S.*, 1935, 1607.
54. Hughes, LeFevre and LeFevre *Ibid.*, 1937, 202.
55. Koelsch .. .. *J. Am. C. S.*, 1933, 3885.
56. Barnett, Goodway and Watson *Ber.*, 1933, 1876.
57. Bergmann and Berlin .. *J. Am. C. S.*, 1940, 316.
58. Lothrop .. .. *Ibid.*, 1939, 2115.
59. German Patent .. 350293; *Friedlaender, Fortschritte der Teerfarben industrie*, **18**, 559.
60. Späth and Pailer .. *Ber.*, 1934, 1212.
61. Rangaswami and Seshadri *Proc. Ind. Acad. Sci.*, 1937, **6A**, 112.
62. Späth and Pailer .. *Ber.*, 1935, 941.
63. Limaye and Gangal .. *Rasayanam*, 1936, 15.

64. Rangaswami and Seshadri *Proc. Ind. Acad. Sci.*, 1938, **7A**, 8.
65. Rao .. .. *Ibid.*, 1936, **4A**, 687.
66. Rangaswami and Seshadri *Ibid.*, 1939, **9A**, 7.
67. Wittig, Baugert and Reichert *Ann.*, 1925, 184.
68. Baker .. .. *J. C. S.*, 1934, 73.
69. Rangaswami and Seshadri *Proc. Ind. Acad. Sci.*, 1939, **9A**, 1.
70. Rao, Sastri and Seshadri .. *Ibid.*, 1939, **9A**, 22.
71. Rangaswami and Seshadri *Ibid.*, 1939, **9A**, 526.
72. Gilman and Van Ess .. *J. Am. C. S.*, 1939, 1365.
73. ———— .. *Ibid.*, 1939, 3146.
74. LeFevre and LeFevre .. *J. C. S.*, 1937, 196.
75. Sandin, Gillies and Lynn .. *J. Am. C. S.*, 1939, 2919.
76. Orndorff and Hemmer .. *Ibid.*, 1927, 1272.
77. Hewitt and Woodford .. *J. C. S.*, 1902, 893.
78. Ingraffia .. *Gazz. Chim. Ital.*, 1932, 781.
79. Mills and Smith .. *J. C. S.*, 1922, 2724.
80. LeFevre and LeFevre .. *Ibid.*, 1935, 1470.

THE KINETICS OF THE MUTAROTATION OF AMINOMETHYLENE-*d*-CAMPHOR

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The mutarotation of aminomethylene-*d*-camphor in glacial acetic acid and in aqueous acetic acid solutions has been studied in this paper.

Aminomethylene-*d*-camphor was first prepared by Bishop Claisen and Sinclair.[1] Later Singh and Bhaduri[2] studied its rotatory dispersion in several solvents. Iminomethylene-*d*-camphor was also prepared by Bishop Claisen and Sinclair (*loc. cit*), but the yield was very poor. Singh and Bhaduri (*loc. cit*) obtained this substance in better yield by the condensation of aminomethylene-*d*-camphor with oxymethylene-*d*-camphor. We have now discovered that it can be prepared very simply by dissolving aminomethylene-*d*-camphor in glacial acetic acid: the conversion takes place in a short time and the yield is quantitative. The change is complete in the cold (35°) within 1 hour and 40 minutes (Table I). The reaction is much hastened on boiling and the conversion is complete within 5 minutes. It has been further observed that if aminomethylene-*d*-camphor is heated above its melting point, ammonia is given off and iminomethylene-*d*-camphor is formed.

As the conversion of aminomethylene-*d*-camphor into iminomethylene-*d*-camphor takes place with measurable velocity in glacial acetic acid solution in the cold, and is accompanied by a change in its rotatory power, it has been found possible to determine the velocity constant of the reaction (Table I). The chemical reaction is found to be monomolecular and the mean value of k, the velocity constant, varies from $5{\cdot}94 \times 10^{-2}$ to $6{\cdot}11 \times 10^{-2}$ at four different concentrations ranging from about 0·4% to 1·6%.

The mutarotation of aminomethylene-*d*-camphor in acetic acid of 90%, 80% and 75% concentration has also been determined. Whereas mutarotation in glacial acetic acid solution is accompanied by a rise in rotatory power, there is first a rise followed by a fall in rotatory power in aqueous acetic acid solution (Tables II and IV). The small rise in rotatory power in aqueous

[1] *Ann.*, 1894, **281**, 395.

[2] *J. Ind. Chem. Soc.*, 1932, **9**, 109.

acetic acid solution occurs in the first six or seven minutes of making up the solution (Tables II and IV), and after this brief period there is a gradual fall in rotation which becomes constant, but the value is different in the case of solutions of varying strength of acetic acid. If the polarimetric observation is delayed for about 7 minutes after making up the solution, the initial rise in rotatory power is not observed (Table III). The reaction in aqueous acetic acid solution does not follow the monomolecular equation. It is, therefore, clear that the reaction takes a somewhat different course in aqueous acetic acid solution. The reason for this anomalous behaviour is not, at present, quite clear, and further work for its elucidation is required. Whether the presence of water in acetic acid brings about racemisation, and may thus explain the erratic changes in rotatory power is still a moot point. Iminomethylene-*d*-camphor prepared from aminomethylene-*d*-camphor in glacial acetic acid solution and in dilute acetic acid (90% and 80%) has the same rotatory power in ethyl alcohol (Table V), but the yield in each case is different. It is maximum in glacial acetic acid and diminishes with its dilution with water.

Experimental

Aminomethylene-*d*-camphor (1 gr.) is heated with 25 c.c. of glacial acetic acid for about 10 minutes. Water is then added to the solution when iminomethylene-*d*-camphor is thrown down. It is crystallised from ethyl alcohol as needles, m.p. 216°–218°. The yield being over 0·9 gr. is almost quantitative. The lævo and racemic varieties of iminomethylene-camphor are obtained in the same way from *l*– and *dl*- forms of amino-methylene-camphor, m.p. 216–218° as in the case of the *d*-isomeride.

The solution for polarimetric observations was made by dissolving the given weight of aminomethylene-*d*-camphor in the solvent which had been previously kept in the thermostat at 35° C. The thermostat was heated electrically and its temperature was controlled by means of a toluene regulator. The temperature was read with a Beckmann thermometer, and was correct within 1/50th of a degree centigrade. The rotatory power was determined in a 2-dcm. jacketed tube, through which water was circulated by means of an electrically-driven pump from the thermostat. The polarimeter was of the Adam Hilger triple field type, which carried a D.V. spectroscope in the eye-piece. A vertical slit was used as a source of light at the polariser end, which was illuminated with a mercury arc.

The value of k, the velocity constant, is calculated from the monomolecular equation,

$$k = \frac{2 \cdot 303}{t_y - t_x} \log \frac{[\alpha]_x - [\alpha]_\infty}{[\alpha]_y - [\alpha]_\infty},$$

the time being expressed in minutes.

TABLE I

Solvent: *Glacial Acetic Acid*

I Series: Concentration, g/100 c.c. = 0·3904

Time	$[\alpha]^{35°}_{Hg\ 5461}$	K × 10^{-2}	Time	$[\alpha]^{35°}_{Hg\ 5461}$	K × 10^{-2}
Initial	Not observed	..	15′ 30″	611·2°	6·10
6′ 5″	503·3°	..	16′ 35″	620·4	6·10
7′	516·6	5·90	17′ 35″	628·4	6·10
8′	530·4	5·94	19′	638·8	6·02
9′	543·3	5·92	21′	652·2	6·10
10′	555·8	6·03	24′ 10″	669·8	5·89
11′ 15″	569·9	5·86	25′ 10″	674·9	6·14
12′ 15″	580·4	5·83	29′	691·4	5·97
13′ 15″	590·4	5·87	1 hr. 40′	755·6	..
14′ 30″	602·1	5·88	∞ (160 hrs.)	755·6	..
				Mean ..	5·98

II Series: Concentration, g/100 c.c. = 0·8296

Time	$[\alpha]^{35°}_{Hg\ 5461}$	K × 10^{-2}	Time	$[\alpha]^{35°}_{Hg\ 5461}$	K × 10^{-2}
Initial	Not observed	..	18′	609·3°	5·94
4′ 40″	427·9°	..	19′ 20″	620·8	6·11
6′	453·2	6·01	23′ 20″	649·7	5·99
9′	503·9	6·03	24′ 20″	655·7	5·83
10′	518·3	5·87	25′ 40″	663·4	5·95
13′	557·8	6·05	26′ 45″	669·2	5·95
14′ 30″	575·1	6·08	29′	680·4	5·90
16′	590·6	5·96	∞	756·4	..
17′	600·3	6·11		Mean ..	5·98

III Series: Concentration g/100 c.c. = 1·2144

Time	$[\alpha]^{35°}_{Hg\ 5461}$	K × 10^{-2}	Time	$[\alpha]^{35°}_{Hg\ 5461}$	K ×·10^{-2}
Initial	Not observed	..	15′	598·6°	6·06
4′	450·3°	..	16′ 45″	613·5	5·62
5′	467·6	5·78	17′ 45″	621·7	5·87
6′	484·5	5·99	19′	631·6	6·04
7′ 20″	505·8	6·10	20′	639·0	6·04
8′ 25″	522·2	6·23	21′	645·8	5·97
9′ 40″	539·4	6·06	24′	664·5	6·10
10′ 40″	551·9	5·81	25′	669·8	5·85
11′ 40″	563·6	5·87	30′	691·7	5·74
12′ 40″	574·8	5·94	∞	757·6	..
13′ 40″	585·2	5·87		Mean ..	5·94

IV Series: Concentration, g/100 c.c. = 1·6488

Time	$[\alpha]^{35°}_{Hg\ 5461}$	K × 10^{-2}	Time	$[\alpha]^{35°}_{Hg\ 5461}$	K × 10^{-2}
Initial	Not observed	..			
2′ 40″	433·6°	..	15′ 15″	606·5°	5·94
4′	458·9	6·08	17′ 35″	629·0	6·05
5′	476·1	5·94	18′ 55″	636·5	5·85
6′ 20″	498·2	6·11	20′	645·3	6·95
8′ 40″	532·2	6·01	22′	658·1	6·01
10′ 40″	558·0	6·07	23′	664·1	6·20
13′	584·8	6·17	∞	758·1	..
				Mean ..	6·11

Table II

Solvent: 90% *Acetic Acid*

Concentration, g/100 c.c. = 0·3672

Time	$[\alpha]^{35°}_{Hg\ 5461}$	Time	$[\alpha]^{35°}_{Hg\ 5461}$
Initial	Not observed		
3′ 10″	612·7°	20 hrs.	571·9°
4′	631·8	44 ,,	544·7
7′ 15″	640·0	67 ,,	537·9
8′ 10″	633·2	92 ,,	510·6
9′	626·4	164 ,,	463·0
16′	623·6	188 ,,	456·1
32′ 20″	612·7	212 ,,	456·1
		236 ,,	456·1

Table III

Solvent: 80% *Acetic Acid*

Concentration, g/100 c.c. = 0·3788

Time	$[\alpha]^{35°}_{Hg\ 5461}$	Time	$[\alpha]^{35°}_{Hg\ 5461}$
Initial	Not observed		
5′ 50″	572·9°	18 hrs.	402·6°
6′ 50″	567·6	28 ,,	376·2
10′	559·7	42 ,,	366·9
17′ 5″	554·4	93 ,,	348·5
1 hr. 44′	534·6	139 ,,	344·5
3 hrs. 8′	514·8	221 ,,	333·9
5 ,, 33′	493·7	317 ,,	332·6
		365 ,,	332·6

TABLE IV

Solvent: 75% *Acetic Acid*

Concentration, g/100 c.c. = 0·3788

Time	$[\alpha]^{38°}_{Hg\ 5461}$
Initial	Not observed
3′ 30″	510·8°
4′ 30″	521·5
6′ 30″	516·1
12′ 30″	514·8
17′ 30″	513·5
1 hr. 23′	493·8
3 hrs. 30′	468·6
22 ,, 47′	349·8
131 ,,	297·0
151 ,,	297·0

TABLE V

Solvent: *Ethyl Alcohol*

Concentration, g/100 c.c. = 0·4360

Iminomethylene-*d*-camphor prepared from	$[\alpha]^{35°}_{Hg\ 5461}$
Glacial Acetic Acid Solution ..	636·6°
90% ,, ,, ..	634·1
80% ,, ,, ..	632·4

The initial time of reading, given in the Tables, from the commencement of the solution, was not the same, but varied in different experiments.

Further work on this compound and its lævo-isomeride is in progress at Allahabad.

KINETICS OF SOL-GEL TRANSFORMATION

Part V. The Influence of Different Coagulating Electrolytes on the Setting of Ferric Phosphate Gel

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In previous publications of this series,[1] the authors have studied the expression $\log S = \log R + p \log C$, where S is the inverse setting time of the jelly when coagulation has been affected with an electrolyte of concentration C. R and p are constants, the significance of which has been mentioned in previous papers. We have shown that the expression is valid for almost all the jellies obtained by slow gelation of sols in presence of varying concentrations of electrolytes. The influence of dilution, temperature and purity of sols on the setting of these jellies has been investigated already. In the present communication, we have studied the influence of various coagulating ions on the setting of ferric phosphate jellies.

The quantitative expression for the coagulating power of electrolytes, especially with reference to the valency of coagulating ions, was given by Whetham.[2] According to him, if discharge requires the presence of ions of opposite charge in the vicinity of the particle, there must be present simultaneously 2 trivalent, 3 divalent or 6 monovalent ions. Since the probabilities for simultaneous presence are proportional to the corresponding powers of the concentrations, Whetham arrived at the following formula for the flocculating concentrations of monovalent, divalent and trivalent ions, c_1, c_2 and c_3:

$$1/c_1 : 1/c_2 : 1/c_3 = 1 : x : x^2.$$

Chakravarti, Ghosh and Dhar[3] have modified the Whetham's equation slightly. According to them, if $N_1, N_2, N_3, \cdots N_x$ be the precipitating concentrations of uni-, bi-, tri-,...x-valent ions, then

$$N_1 : N_2 : N_3 : \cdots : N_x = 1 : \frac{1}{2}\alpha : \frac{1}{3}\alpha^2 : \cdots : \frac{1}{x}\alpha^{x-1},$$

where $\alpha = e^{\frac{-qe/Dr}{KT}}$.

These expressions are only valid when the coagulation process does not involve any complication and is guided by the mere electric attraction between the colloidal particle and the ion. The possible complications in the case of an ordinary coagulation are the adsorption of similarly charged ion, the marked adsorbability of the precipitating ion and the large differences in the ionic velocity of the coagulating ions. When applied to the coagulation processes leading to the formation of a jelly, all these expressions are bound to fail. The process of jelly formation starts with the charge neutralisation and the formation of secondary or tertiary aggregates from the primary ones, and then continues through the regular imbibition of water molecules round the completely or partially discharged colloidal aggregates, and finally ends into the formation of a jelly-mesh which entangles the whole of the dispersing phase. Most of these stages directly or indirectly depend on the valency of coagulating ions. It is difficult to find out the exact conditions of aggregation and still more difficult would be to assign quantitative relationships to the surficial and structural hydration. According to Rice,[4] colloidal particles do not aggregate if $\frac{4\pi\sigma^2 r}{D} > r_0^{\infty}$, where σ is the surface density of electric charge, r the thickness of the double layer, D the dielectric constant of the medium and r_0^{∞} is the non-electrical surface tension of the colloid particle. Rice has also shown that aggregation will become very rapid when a definite σ is reached. The surface density of electric charge, σ, is bound to be effected by the adsorbed solvent layers round the partially discharged colloidal particle. The non-electrical surface tension of the colloidal particle in such cases would tend to merge into the surface tension of the solvent medium.

Experimental

We have carried experiments with different coagulating electrolytes, such as potassium chloride, potassium sulphate, potassium citrate, calcium chloride and barium chloride. The ferric phosphate sols were prepared by the usual Holmes method by adding potassium dihydrogen phosphate solution to a solution of ferric chloride in concentrations short of precipitation and dialysing the sol. The values of P and log R have been calculated from the observations given below.

Concentration of the sol = 62·92 g. ferric phosphate per litre. Purity of the sol Fe/Cl = 0·3873/0·0765 = 5·06. Amount of sol taken = 3 c.c. and the total volume = 5 c.c.

The above results have been summarised in Table II which show that the values of p and log R are not exactly the same and thus it is evident that ferric phosphate does not adsorb chloride, bromide and nitrate ions to the same extent, or these ions have some other more complicated preferential influence. The influence of different coagulating ions has been shown in Fig. 1.

TABLE I

With uni-univalent electrolytes

Conc. of electrolyte used (C)	log C	Setting time, θ (secs.)	log S ($-\log\theta$)	The values of p and log R calculated
		With 1·5 *N-KCl*		
(1) 0·51 N	−0·2924	702	−2·8463	From (1) and (2)— $p=3\cdot24$; log R = −1·90
(2) 0·33	−0·4815	2880	−3·4594	From (1) and (3)— $p=3\cdot26$; log R = −1·89
(3) 0·27	−0·5686	5580	−3·7466	Mean value— $p=3\cdot25$; log R = −1·90
		With N-KNO$_3$		
(1) 0·40 N	−0·3979	4080	−3·6107	From (1) and (3)— $p=3\cdot36$; log R = −2·27
(2) 0·38	−0·4202	4860	−3·6866	From (2) and (3)— $p=3\cdot35$; log R = −2·28
(3) 0·33	−0·4815	7800	−3·8921	Mean value— $p=3\cdot35$; log R = −2·28
		With 1·5 *N-KBr*		
(1) 0·60 N	−0·2218	3960	−3·5977	From (1) and (3)— $p=2\cdot75$; log R = −2·99
(2) 0·57	−0·2441	4560	−3·6590	From (2) and (3)— $p=2\cdot75$; log R = −2·99
(3) 0·48	−0·3188	7320	−3·8645	Mean value— $p=2\cdot75$; log R = −2·99

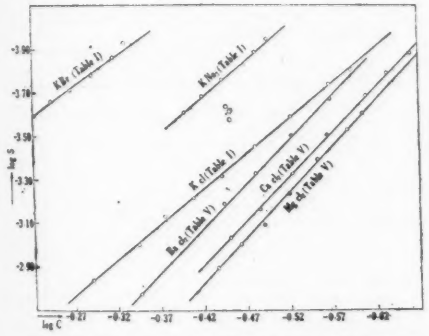

FIG. 1. Influence of different coagulating ions

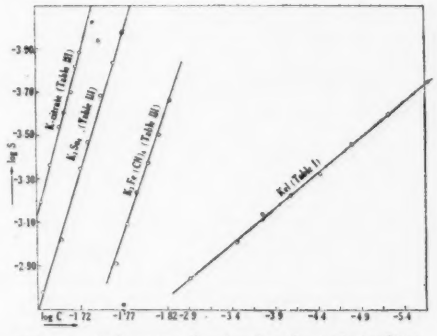

FIG. 2. Influence of uni-polyvalent electrolytes

TABLE II

Electrolyte	p	log R
1·5 N-KCl	3·25	− 1·90
N-KNO_3	3·35	− 2·28
1·5 N-KBr	2·75	− 2·99

TABLE III

With uni-polyvalent electrolytes

Conc. of electrolyte used (C)	log C	Setting time, θ (secs.)	log S ($-\log \theta$)	The values of p and log R calculated
		With N/10-K_2SO_4		
(1) 0·021 N	−1·6778	608	−2·7839	From (1) and (2)— p=12·98; log R=18·99
(2) 0·0186	−1·7305	2940	−3·4683	From (1) and (3)— p=12·90; log R=18·86
(3) 0·017	−1·7696	9300	−3·9685	Mean value— p=12·94; log R=18·93
		With 0·0529 N-Potassium citrate		
(1) 0·02116 N	−1·6745	1560	−3·1931	From (1) and (3)— p=14·67; log R=21·37
(2) 0·02063	−1·6855	2280	−3·3579	From (2) and (4)— p=14·66; log R=21·35
(3) 0·01957	−1·7085	4920	−3·6920	
(4) 0·01904	−1·7203	7380	−3·8681	Mean value— p=14·66; log R=21·36
		With 0·0455 N-$K_3Fe(CN)_6$		
(1) 0·01683 N	−1·7739	1252	−3·0976	From (1) and (2)— p=11·27; log R=16·89
(2) 0·01592	−1·7980	2340	−3·3692	From (1) and (3)— p=11·29; log R=16·93
(3) 0·01501	−1·8236	4560	−3·6590	Mean value— p=11·28; log R=16·91

The influence of uni-polyvalent electrolytes has been summarised in Table IV. In Fig. 2 are given the graphs showing the influence.

TABLE IV

Electrolyte	p	log R
1·5 N-KCl	3·25	− 1·90
N/10-K_2SO_4	12·94	18·93
0·0529 N-K-citrate ..	14·66	21·36
0·0455 N-$K_3Fe(CN)_6$ ..	11·28	16·91

It is clear from these figures that the values of p and log R markedly increase if the jelly is formed by the uni-bivalent ion. The difference between uni-bivalent and uni-trivalent is not so marked as between uni-monovalent and uni-bivalent. The ferrocyanide ion does not fall into the series, probably due to the chemical reactivity with the iron sol.

TABLE V

With poly-univalent electrolytes

Conc. of electrolyte used (C)	log C	Setting time, θ (secs.)	log S ($-\log\theta$)	The values of p and log R calculated
		With 1·36 *N–*$CaCl_2$		
(1) 0·3536 N	−0·4515	1104	−3·0429	From (1) and (3)— p=4·06; log R=−1·21
(2) 0·2992	−0·5240	2160	−3·3345	From (2) and (3)— p=4·09; log R=−1·19
(3) 0·2448	−0·6112	4920	−3·6920	Mean value— p=4·07; log R=−1·20
		With 1·5 *N–*$BaCl_2$		
(1) 0·45 N	−0·3468	608	−2·7839	From (1) and (2)— p=4·12; log R=−1·35
(2) 0·30	−0·5229	3240	−3·5105	From (1) and (3)— p=4·02; log R=−1·39
(3) 0·27	−0·5686	4740	−3·6758	Mean value— p=4·07; log R=−1·37
		With 1·075 *N–*$MgCl_2$		
(1) 0·3655 N	−0·4371	798	−2·9020	From (1) and (3)— p=4·21; log R=−1·06
(2) 0·3440	−0·4634	1020	−3·0086	From (2) and (3)— p=4·23; log R=−1·05
(3) 0·2472	−0·6069	4140	−3·6170	Mean value— p=4·22; log R=−1·05

The influence of poly-univalent electrolytes has been summarised in the following table:

TABLE VI

Electrolyte	p	log R
1·5 N-KCl	3·25	−1·90
1·36 N-$CaCl_2$	4·07	−1·20
1·5 N-$BaCl_2$	4·07	−1·37
1·075 N-$MgCl_2$	4·22	−1·05

As is expected, the values of p and log R do not much change with the valency of the positively charged ions as the sol itself is positively charged.

Discussion

From the above tables we see that in case of uni-univalent electrolytes such as potassium chloride, potassium nitrate and potassium bromide, the values of p and log R do show only a slight variation. The small differences are due to the specific nature of different ions which are not adsorbed by ferric phosphate to the same extent. The uni-polyvalent electrolytes as potassium chloride, potassium sulphate and potassium citrate show a marked change

in the values of p and log R, while in the case of potassium ferricyanide, the values of these constants lie between those for potassium chloride and potassium sulphate. It seems that this is due to the chemical reaction taking place between the sol and the electrolyte as it is evident from the change of colour exhibited during gelation. The gelation of ferric phosphate sol qualitatively obeys the Schulze-Hardy law. The behaviour of poly-univalent electrolytes as calcium chloride, barium chloride and magnesium chloride is practically the same and the values of p and log R do not show much change. The constants in the case of poly-univalent electrolytes are a little higher than in the case of uni-univalent electrolytes.

The jelly formation of ferric phosphate sol in this respect closely resembles the coagulation of positively charged ferric hydroxide sol. It is interesting to note that the results obtained by Freundlich, Weiser and Dhar on positively charged ferric hydroxide sol are in fair agreement with ours. From Freundlich's observations,[5] the order of precipitating power of the anions is dichromate > sulphate > hydroxide > benzoate > chloride > nitrate > bromide > iodide. Dhar[6] has obtained from this sol the following series:

Ferricyanide > citrate > oxalate > sulphate > hydroxide > nitrate > chloride.

No work has been done in this line on the coagulation of ferric phosphate and arsenate sols, but it is expected that these sols would also behave similarly. We have shown that gelation is also essentially a coagulation process and therefore, similar results are expected in gelation too. From the results recorded in the previous tables, the values of log R are in the following order:

With anions: citrate > sulphate > ferricyanide* > chloride > nitrate > bromide.

With cations: magnesium > calcium > barium > potassium. The values of p are in the following order for the ferric phosphate sol.

K-citrate > K_2SO_4 > $K_3Fe(CN)_6$ > $MgCl_2$ > $BaCl_2$ > $CaCl_2$ > KNO_3 > KCl > KBr. The difference in the value of p is very much marked only when we proceed from KCl to K_2SO_4 or to K-citrate, while in other cases the values are almost the same.

By coagulating or flocculating power is usually meant the concentration of electrolyte (expressed in moles or millimoles per litre) necessary to precipitate the sol completely in a stated time. The gelation power of an electrolyte can also be similarly defined in terms of the concentration of electrolyte necessary to set the sol to a gel in a stated time. In order to set a sol in

* Anomalous due to chemical reaction.

time S, let the concentration of the monovalent electrolyte be C_1, so that

$$S = \log R + p \log C_1.$$

The sol with the same characteristics, p and R, would require the concentration C_2 to set the sol to a jelly in the same time S with the polyvalent electrolyte. If the two concentrations are related according to Whetham or some other general law so that $C_1 = \alpha C_2^r$, where r denotes some power depending upon the valency of the ion, the gelation time S would be given by:

$$S = \log R + p \log (\alpha C_2^r)$$

or

$$S = \log R + p \log \alpha + r.\, p \log C_2.$$

Thus the constant log R is replaced by another constant $\log R + p \log \alpha$ and the constant p is replaced by another constant $r.\, p$. The variations observed in the values of log R and p when gelation is affected with different ions as recorded in the previous tables qualitatively agree with these assumptions. The quantitative differences are due to the influence of the similarly charged ions, different adsorbabilities and other factors which do not make the results exactly comparative.

Summary

In continuation with the previous work, the authors have studied the influence of different coagulating ions on the setting of ferric phosphate jellies. The values of p, the jelly characteristic and R the rate constant in the equation $\log S = \log R + p \log C$ do not change much with uni-univalent electrolytes. The slight variations with chloride, bromide and nitrate ions are due to the different adsorbabilities of these ions by ferric phosphate. When the jelly formation is affected with uni-polyvalent ions the marked variations are observed consistent with Whetham's law, or any other generalized expression. With poly-univalent electrolytes, the values of p and log R do not markedly change as the sol itself is positively charged.

In the end, the authors are grateful to Prof. N. R. Dhar for his interest throughout the work.

REFERENCES

1. Prakash and Dube .. *Z. anorg. Chem.*, 1932, **208**, 163.
   Dube .. *Ibid.*, 1934, **217**, 284.
   ——— and Prakash .. *Proc. Ind. Acd. Sci.*, 1940, **11**, 318.
   Dube .. *Ibid.*, 1940, **11**, 331.
2. Whetham .. *Phil. Mag.*, 1899, **48** (5), 474.
3. Chakravarti, Ghosh and Dhar *J. Phys. Chem.*, 1930, **34**, 326.
4. Rice .. *Ibid.*, 1926, **30**, 189, 1660.
5. Freundlich .. *Kapillarchemie*, 1909, 352, 358.
   Weiser .. *J. Phys. Chem.*, 1920, **24**, 641.
6. Dhar .. *Ibid.*, 1924, **28**, 313.

MAGNETISM OF STRONTIUM

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1. Introduction

A comprehensive survey of the magnetic properties of elements was first carried out by Honda (1910) and Owen (1912). The magnetic susceptibilities of nearly sixty elements were measured at temperatures ranging from that of liquid air to about 1200° C. These important investigations have been supplemented by those of later workers. The results of these observers have formed the basis for theoretical investigations on the properties of metals and non-metals.

A metal may be considered to be built up of a lattice of metallic ions, the remaining electrons of the individual atoms being considered free or partly bound in accordance with their energy values. Pauli (1927) considered these electrons to constitute an electron gas and deduced the following expression for the paramagnetic susceptibility $(\chi_A)_e$ of such electrons in a gram atom of the metal.

$$(\chi_A)_e \times 10^6 = 48 \cdot 17\ q/V_0$$

where q is the number of free electrons per atom and V_0 the width in volts of the energy band occupied by the electrons in the completely degenerate state. Landau (1930) and others showed that the curvature of the paths of the free electrons in a magnetic field would be associated with a diamagnetic susceptibility numerically equal to one-third of the paramagnetic susceptibility. This gives for $(\chi_A)_e$ the expression,

$$(\chi_A)_e = 32 \cdot 11 \times \frac{q}{V_0}.$$

For perfectly free electrons, V_0 is of the order of several volts. The effect of the periodic potential field due to the lattice ions will be to narrow the bands but the above equation will still be applicable as an approximation. The diamagnetism of bound electrons has been discussed by Peierls (1933). When the atom has only one loosely bound electron, only one band is to be considered. This is found to be the case with the alkali metals. The narrower the band, the greater will be the number of quantum states per unit energy range and the larger the paramagnetism. In the case of the alkaline earth

elements, an overlapping of the bands due to the two valence electrons should occur, since otherwise the solid would be non-conducting. The greater the overlap, the larger will be the paramagnetism.

The electrons in the closed groups in the atoms will give rise to a normal diamagnetic effect. The gram atomic susceptibility χ_A of the element is the sum of $(\chi_A)_i$, the susceptibility per gram atom of the ion and $(\chi_A)_e$.

The magnetic susceptibilities of calcium, strontium and barium were first determined by Owen (1912). He obtained for the specific susceptibility of these elements the values of $+1{\cdot}10$, $-0{\cdot}2$ and $+0{\cdot}93$.* The metals used in Owen's investigations had a fairly large iron content. To allow for such ferromagnetic impurity, the susceptibility of an element was determined at different field strengths. The specific susceptibility χ_P of the pure specimen could be represented by the expression $\chi_i = \chi_P + \frac{\sigma_m}{H}$ where χ_i is the specific susceptibility of the impure element, σ the specific intensity of magnetization of the ferromagnetic impurity, m the mass of this impurity present in a gram of the substance and H the intensity of the magnetic field. Honda and Owen drew for every element investigated, a graph between χ_i and H. By extrapolating this graph, the value of the specific susceptibility at infinite field strength was determined. This value gave the corrected specific susceptibility χ_P.

If the iron content in a substance is negligibly small, the χ, H graph will be very nearly parallel to the axis of H. Owen's results for calcium, strontium and barium show a very large ferromagnetic content, the χ, H graphs being very steep. Hence the specific susceptibility values obtained by extrapolating such graphs are likely to be vitiated by errors of extrapolation. Owen's results show that whereas calcium and barium are paramagnetic, strontium appears exceptional in being diamagnetic. Two specimens of strontium were studied by Owen, the range of field-strength being from about 13 to 26 kilogauss. The specific susceptibility for one of the specimens varied from about $+6{\cdot}4$ to about $+3{\cdot}4$ in the above mentioned range of field strength. In the case of the other specimen this variation was from $+2{\cdot}7$ to $+1{\cdot}2$. Thus the observed specific susceptibilities of strontium were all paramagnetic.

Stoner (1934) drew attention to the possibility of an overcorrection for the relatively large iron content, resulting in a diamagnetic value for strontium. The present investigation was undertaken with a view to examine this problem. A careful thermomagnetic examination of strontium has also

* All susceptibility values in this paper are given in 10^{-6} unit.

been made. Owen studied the specific susceptibility of this element at different temperatures ranging from about $-160°$C. to $+15°$C. and found no variation in this temperature range. But the susceptibility of the specimen was about $+8$ and measurements seem to have been made at different temperatures only at one field strength.

Lane (1933) studied the specific susceptibility of barium in the range of temperatures 20° C. to 400° C. The value increased from $+0{\cdot}145$ at 20° C. to $+0{\cdot}415$ at 400° C. A slight discontinuity in the χ, T curve at about 350° C. was observed. A change of slope of the curve connecting electrical resistance and temperature is also found at about 350° C. This result may be explained if it is assumed that the top of the Fermi distribution occurs in a region where the bands corresponding to the two valence electrons overlap.

2. *Experiment*

The metal available was a pure specimen of strontium from Merck. A spectroscopic analysis showed the presence of traces of calcium and lead. A chemical examination was made by dissolving a known weight of strontium in hydrochloric acid and precipitating the sulphate. The purity of the specimen was found to be not less than 99·8%.

The specific susceptibility of strontium was determined by the Curie method. Small bulbs containing 20 to 60 mg. of strontium were prepared in the following manner. A pyrex glass tube having a diameter of about 5 mm. was blown to have the shape shown in Fig. 1. After thoroughly cleaning and drying the tube, a suitable quantity of strontium was introduced into the tube. The end A was connected to a high vacuum equipment and the pressure brought down to 10^{-4} cm. of mercury. The tube AE was warmed with a bunsen burner in order that traces of paraffin oil (into which the given specimen of strontium was immersed) might evaporate away. The metal above the constriction at B was then heated by a blow-pipe flame. By jerking the tube vigorously, the molten metal was made to pass through the constrictions B and D into the spherical bulb E. Any oxide film on the metal was removed by the constrictions. The metal which collected in E possessed a bright metallic lustre. The tube was finally sealed off at D, the molten glass being drawn into the form of a hook to enable the bulb E to be suspended during the magnetic measurements.

The electromagnet used was a large one of the Pye type. The pole-pieces of diameter 5 cm. were kept suitably inclined to give rise to a non-uniform field. The electromagnet was capable of carrying a current of about 15 amperes. Since the maximum current used in the present investigation

was only 6 amperes the heating of the coils was very little. The currents were measured with an ammeter of the Cambridge Scientific Company, reading accurately to 0·05 ampere and by estimation to 0·005 ampere. The deflections were read by a lamp and scale arrangement.

The retorsion method was adopted. In the presence of the magnetic field the bulb containing the specimen under investigation was brought to the same position as could be judged by the spot of light on the scale.

The standard substance used was water, the specific susceptibility of which was assumed to be $-0{\cdot}72$ at 30° C.

The bulbs were weighed with a Sauter's balance correctly to within 0·1 mg. After the magnetic experiments, the bulbs were broken open. The metal was dissolved in dilute nitric acid. The magnetic deflections corresponding to the bulbs were then determined after drying them in a vacuum desiccator for a day. The masses of the metal specimens varied from 20 to 60 mg.

It may be shown that if d_s and d_w are the deflections produced by masses m_s and m_w of strontium and water respectively

$$\frac{d_s}{d_w} = \frac{m_s\chi_s - k_a v_i}{m_w\chi_w - k_a v_i'}$$

where χ_s and χ_w are the specific susceptibilites of strontium and water respectively, k_a is the volume susceptibility of air at the room temperature and v_i and v_i' are the internal volumes of the metal and water bulbs.

During the determination of the specific susceptibility of strontium at high temperatures, the volume susceptibility k_T of air at any absolute temperature T was determined from the relation $k_T/T^2 =$ a constant. The volume susceptibility of air at N.T.P. was assumed to be $+0{\cdot}029$.*

3. *Results*

The results obtained with 9 specimens are given in Table I.

The values of the specific susceptibility at different field currents are given in column 4. The last column gives the specific susceptibility of the metal obtained by drawing χ, 1/H graph and extrapolating it to infinite field strength. The average specific susceptibility of strontium is found to be $+1{\cdot}05 \pm 0{\cdot}03$. The element is thus found to be paramagnetic, contrary to the observations of Owen (1912) who obtained the value of $-0{\cdot}2$ for the metal. The gram atomic susceptibility of the metal is therefore $+92{\cdot}0$.

The specific susceptibility of strontium was determined at different temperatures ranging from 0 to 260° C. The bulb containing strontium was

* *Int. Crit. Tables*, 1929, **6**, 354.

TABLE I

Bulb No.	Mass (mg.)	Current (amperes)	X	X (extrapolated)
1	28·7	2	5·15	1·02
		3	3·42	
		4	2·34	
		5	2·10	
2	42·9	2	4·14	1·02
		3	2·75	
		4	2·11	
		5	1·84	
		6	1·76	
3	34·5	2	3·62	1·03
		3	2·50	
		4	1·81	
		5	1·69	
4	54·5	2	3·41	1·02
		3	2·35	
		4	1·78	
		5	1·63	
5	64·8	2	2·80	1·08
		3	2·00	
		4	1·63	
		5	1·51	
		6	1·42	
6	40·6	2	2·02	1·08
		3	1·61	
		4	1·38	
		5	1·35	
7	51·8	2	1·91	1·06
		3	1·53	
		4	1·38	
		5	1·32	
8	56·3	2	1·64	1·06
		3	1·35	
		4	1·25	
9	61·0	2	1·83	1·06
		3	1·50	
		4	1·33	
		5	1·24	

heated by enclosing it inside an electric heater made by winding constantan wire on an asbestos cylinder. The pole pieces were cooled by cotton wads drenched with iced water. The magnetic field inside the heater was in no way disturbed by the heating coils.

A preliminary investigation was carried out by enclosing inside the heater a thermometer, reading to 340° C. and one junction of a thermo-electric couple made of silver and constantan wires. The terminals of the thermo-couple

were connected to a sensitive pointer galvanometer. A graph was drawn between the reading of the galvanometer and the corresponding thermometer reading, by gradually increasing the temperature inside the heater. During the magnetic experiments, the temperature of the heater was determined by using the themocouple. Test experiments showed that temperatures measured in this manner were accurate to within 5°. The specific susceptibility at the temperature of melting ice was determined by enclosing the specimen within a chamber cooled outside by melting ice.

The variation with temperature of the susceptibility of the pyrex glass containers was studied separately. The bulbs were found to possess a diamagnetic susceptibility which was constant in the temperature range investigated.

Fig. 2 shows the graph drawn between the specific susceptibility of strontium and temperature. The specific susceptibility is found to increase from 1·02 at 0° C. to about 1·09 at 65° C. Thereafter the susceptibility decreases gradually to about 0·73 at 260° C.

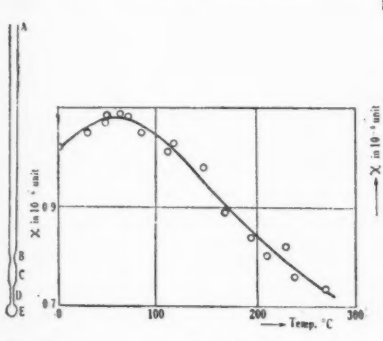

FIG. 1 FIG. 2

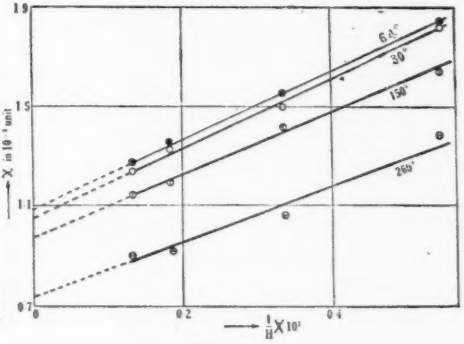

FIG. 3

Fig. 3 shows the graphs between χ and 1/H at temperatures of 30°, 64°, 150° and 260° C. These graphs are presented to show how χ varies with 1/H in the different ranges of temperatures studied. The slope of the straight line graphs is found to decrease appreciably at higher temperatures. One would expect this to take place in view of the decreasing intensity of magnetization of the ferromagnetic impurity at the higher temperatures.

4. Discussion

The gram atomic susceptibility of the metal is found to be $+92{\cdot}0$. If the ionic susceptibility of Sr^{+2} is assumed to be $-15{\cdot}6$ after Kido (1933), we obtain for the contribution to the susceptibility $(\chi_A)_e$ of a gram atom of the

metal by the valence electrons (2 per atom) the value of $+107{\cdot}6$. From the equation

$$(\chi_A)_e = \frac{32{\cdot}1q}{V}$$

where $q = 2$ for the strontium atom, V is found to be $0{\cdot}6$ volt. This measures the width of the occupied energy range in the completely degenerate state of the valence electrons in the metal. This result supports the observation of Stoner (1934) that in the alkaline earth elements, the electron energy bands are much narrower than for free electrons. Our observation brings strontium in a line with calcium and barium so far as their magnetic properties are concerned.

The temperature variation of the specific susceptibility of strontium seems to be of special interest. Considering the Fermi energy distribution of the two overlapping bands, the high value of the specific susceptibility of strontium indicates that the overlapping of the bands must be considerable. The temperature coefficient of susceptibility of a divalent element has been shown (Stoner, 1936) to be dependent in a critical manner upon the relation between $\nu(\epsilon)$ the number of states per unit energy range and the energy ϵ of the overlapping bands. It would be of interest to apply these considerations to strontium in the light of the results explained above.

In magnetic properties, strontium seems to behave like the rare earth elements. It has a comparatively high paramagnetism. A clear account of the spin paramagnetism of the rare earths is given by Wilson (1939, 69). In the absence of a magnetic field, the number of free electrons with their spins along the direction of the field is equal to the number with their spins in the opposite direction. The effect of the magnetic field H is to increase the former and decrease the latter. The reversal of spin increases the kinetic energy of such electrons which go into higher energy states which were unoccupied. It is found therefore that the electrons near the top of the Fermi distribution really contribute to the paramagnetism in these cases.

Stoner (1936 *a*) has derived the following formula for $(\chi_A)_e$ the electronic contribution to the gram atomic susceptibility.

$$(\chi_A)_e \times 10^6 = 64{\cdot}21\, n(V_0)\left[1 + 1{\cdot}222 \times 10^{-8}\, T^2 \left\{\frac{1}{n}\frac{\partial^2 n}{\partial V^2} - \left(\frac{1}{n}\frac{\partial n}{\partial V}\right)^2\right\}_{V = V_0}\right]$$

Here $n(V)$ is the number of states for one direction of spin per atom per volt, T is the absolute temperature and V_0 is the maximum Fermi energy in volts.

The spin susceptibility will increase or decrease with temperature in the low temperature range as the sign of the quantity

$$\left\{\frac{1}{n}\frac{\partial^2 n}{\partial V^2} - \left(\frac{1}{n}\frac{\partial n}{\partial V}\right)^2\right\}_{V=V_0}$$

is positive or negative. If instead of in volts, the energy is expressed in ergs, the above expression changes to

$$\left\{\frac{1}{n}\frac{\partial^2 n}{\partial \epsilon^2} - \left(\frac{1}{n}\frac{\partial n}{\partial \epsilon}\right)^2\right\}_{\epsilon=\epsilon_0}$$

It may be shown that the temperature coefficient of the susceptibility due to electrons in an isolated band will be negative. For in the above expression, the first term may be shown to be negative in such cases and the second term is negative or zero.

When there is overlapping of two bands as in the case of the alkaline earth elements, the sign of the temperature coefficient of susceptibility will depend on the extent of overlapping. The high paramagnetism of strontium shows that this overlapping must be considerable. It is of interest that in exactly such a case the temperature coefficient of the paramagnetism due to electrons assumes importance. The variation of $n(\epsilon)$ as a function of ϵ when the bands overlap considerably may be such that $\frac{\delta^2 n}{\delta \epsilon^2}$ may be positive and sufficiently large when $\epsilon = \epsilon_0$, the maximum Fermi energy. In this case a positive temperature coefficient will be obtained. The positive temperature coefficient obtained by Lane (1933) for the paramagnetic susceptibility of barium could be generally explained on this basis. But the increase is so large that a satisfactory quantitative explanation on these lines could not be given.

If increase of temperature brings about directly or indirectly a displacement of the second band relatively to the other reducing the extent of overlapping, the temperature coefficient may change over from a positive to a negative value. At very large temperatures, the susceptibility should decrease with T for, when the electron behaves classically, we have the volume susceptibility K varying as T^{-1}.

The question arises whether the relative displacement of the second band at temperatures within 100° C. could be brought about directly by temperature variation or by changes in physical properties resulting from the elevation of temperature. Unfortunately data relating to strontium are very meagre and no difinite indication is available under this head.

However, mention may be made of the investigations of Bridgman who studied the electrical resistance of calcium and strontium at 0°, 50° and 100° C. at different pressures. The pressure coefficient of calcium was found to increase with rising temperature. That of strontium decreased very slightly at 0° C. with rise of pressure; but at 50° C., it increased with rise of pressure to 2000–3000 kilograms per sq. cm. then showed a flat maximum and then decreased. At 100° C. the behaviour was like that at 50° except that the maximum was sharper, Mellor (1923, 636). These results show that the behaviour of strontium at 0° C. is different from that at 50° C.

Summary

The specific magnetic susceptibility of strontium has been determined by the Curie method. The value at 30° C. is found to be $+1{\cdot}05 \times 10^{-6}$. A thermomagnetic investigation of the metal showed the specific susceptibility to increase from $1{\cdot}02 \times 10^{-6}$ at 0° C. to $1{\cdot}09 \times 10^{-6}$ at about 65° C. The susceptibility decreased thereafter to $+0{\cdot}73 \times 10^{-6}$ at 260° C. Attention is drawn to the interest which these observations have in the light of the Fermi distribution of energy of the valence electrons of strontium.

REFERENCES

Honda .. *Ann. d. Physik*, 1910, **32**, 1027.
Kido .. *Sc. Rep. Tohoku Univ.*, 1933, **22**, 835.
Landau .. *Z. f. Physik*, 1930, **64**, 629.
Lane .. *Phys. Rev.*, 1933, **44**, 43.
Mellor .. *Treatise*, 1923, **3**.
Owen .. *Ann. d. Physik*, 1912, **37**, 657.
Pauli .. *Z. f. Physik*, 1927, **41**, 81.
Peierls .. *Ibid.*, 1933, **80**, 763.
Stoner .. *Magnetism and Matter*, 1934, 512.
———— .. *Honda Anniversary Volume*, 1936, 293.
———— .. *Proc. Roy. Soc.*, 1936 *a*, **150**, 656.
Wilson .. *Semi-Conductors and Metals*, 1939.

RAMAN EFFECT AND HYDROGEN BONDS

Part I. Mixtures of Esters and Acceptor Molecules

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The hydrogen bond or the binding of two atoms by means of an atom of hydrogen has been successfully employed to give concreteness to such indefinite terms as partial valence, secondary forces, co-ordination, association and ortho-effect. Such a role of hydrogen (secondary forces) seems to have been first postulated by Moore and Winmill[1] to account for the differences in strength between tertiary and quarternary ammonium bases. The idea was developed into 'the hydrogen bond' within the scope of Lewis valence theory by Huggins[2] and Latimer and Rodebush[3] to account for the association of water and for the formation of ions such as HF_2^-. It was extended to organic compounds with special reference to chelate structures by Sidgwick,[4] who considered it as a particular case of Werner's co-ordination theory. This concept of hydrogen bond implies the capacity of hydrogen to assume a co-valency of two. Association between two molecules is represented as –A : H : A′– where A and A′ are the electronegative atoms of the two molecules which the 'H' atom holds together. The physical objections to this idea of co-valency of two for hydrogen, which implies a group of four shared electrons are very strong. The difficulties, however, seem to have been overcome by introducing the idea of resonance[5] between two structures in the first of which the 'H' atom is attached to one and in the second to the other of the two atoms which it holds together (R:H :R′, R: H:R′). Whatever may be the exact details regarding the mechanism of the hydrogen bond, its occurrence is beyond doubt and there is good evidence for the capacity of a hydrogen atom to hold two other atoms together.

Newer methods of investigation have provided extensive experimental material which supports the theory of hydrogen bonds in a remarkable manner. The importance of this subject and the interest evinced by workers in various fields of investigation is clearly indicated by the recent discussions of the Faraday Society.[6] Studies on the crystal structure of both inorganic and organic compounds have revealed several features indicating the existence of hydrogen bonds. The work of Pauling and Brockway,[7] employing the method of electron diffraction, has definitely established the existence

of dimers of carboxylic acids involving hydrogen bonds. But by far the most important contribution to our knowledge of the subject has been made by the investigations of infra-red absorption spectra. Wulf and collaborators[8] have examined the spectra of many organic compounds in solution and noticed the absence of the second harmonic of the OH band in cases where hydrogen bonds were to be anticipated. An account of similar work turned out in Cotton's laboratories in Paris since 1932 is given by Freyman.[9] Buswell, Dietz and Rodebush[10] investigated a large number of compounds using the region of the fundamental hydroxyl band and found the important generalisation that the presence of hydrogen bonds is accompanied by a considerable increase in the absorption and a marked change in the frequency of the band, the shift being in the direction of longer wavelengths. This work has been confirmed by other investigators[11] independently. Walter Gordy and co-workers[12] have made an extensive series of investigations on liquids and binary liquid mixtures and thus obtained information regarding the formation of hydrogen bonds between similar as well as dissimilar molecules. No attempt has, however, been made in this paper to give any exhaustive account of the infra-red studies; only items relevant to the discussion on Raman effect and hydrogen bonds have been included.

In regard to the application of the Raman effect to the study of hydrogen bonds no systematic investigation has so far been reported, though the concept has been utilised by some workers[13] in the past to explain certain peculiarities in the Raman spectra of compounds and binary mixtures observed by them. Since the potentialities of this method are obviously great, the investigations described in this series of communications have been undertaken. The usual procedure adopted in infra-red spectroscopy is to determine the effect of hydrogen bond formation on the absorption of the group which carries the hydrogen, as for example the OH group of alcohols and phenol. It is relatively in very few cases that the effects of the bond on the second group involved, such as the C = O in carbonyl compounds, have been examined. The large amount of data obtained from infra-red studies seems to indicate that hydrogen bond formation is more or less universal in liquids and liquid mixtures of molecules having donor and acceptor atoms. In our investigations attention is confined to cases of hydrogen bond formation where the oxygen of the C = O group of various carbonyl compounds acts as the donor. Such cases may be represented as below:—

$$\rangle C{=}O \rightarrow H{-}O{-}R$$

It readily follows that there should be a weakening of the C = O bond resulting in a lowering of the frequency of the line attributable to this linkage.

In this procedure possibilities of accuracy and definiteness are greater since the Raman line of the C = O is usually bright and sharp and any modifications undergone by it can be easily recorded. On the other hand the utilisation of the OH group is difficult for two reasons, *viz.*, (i) the difficulty of recording the OH band and (ii) the non-existence of any hydroxylic compound devoid of hydrogen bond in it for use as the correct standard.

Hydrogen bonds can be classified broadly under two heads namely, intermolecular and intramolecular hydrogen bonds. In the former, the two atoms linked by the hydrogen belong to different molecules whereas in the latter they are present in the same molecule. Intermolecular hydrogen bonds may further be subdivided as the homo- and the hetero-molecular types according as the union is brought about between similar and dissimilar molecules respectively. These bonds are represented by many American workers by means of dotted lines joining the donor atom and the hydrogen. It seems to be more reasonable to represent them by means of arrows pointing in the direction of the pull of electrons as $> C = O \rightarrow H\text{-}O\text{-}R$. The terms donor and acceptor are used by some[14] in connection with the proton but it appears to be more correct to refer them to the electrons since, according to the ideas advanced by Sidgwick,[5] it is only the electrons that change their positions in the resonance condition. Further, this will be in accordance with the accepted usage of these terms in connection with co-ordinate valency.

The essential requisites for the formation of hydrogen bonds are (i) the existence of ' H ' atoms with the capacity to serve as acceptors and (ii) the presence of atoms having free pairs of electrons, enabling them to act as donors. As examples may be mentioned ' H ' atoms present in hydroxylic and amino compounds under category (i) and oxygen, nitrogen and chlorine atoms under category (ii). Consequently the strength of hydrogen bonds will depend upon the anionoid power of the donor and the cationoid power of the acceptor atoms and a large variation in bond strength is possible.

In this connection it may be recalled that Bernal[15] proposed to distinguish between two types of hydrogen bonds and to call them the hydrogen and the hydroxyl bonds respectively. " In the hydrogen bond the hydrogen atom is attached with almost equal firmness to the two oxygen atoms which it joins, the O—H $\cdots$ O distance being 2·50–2·65 Å corresponding to an energy of the bond of about 8000 cal./ mol. The O–H links in these conditions are greatly weakened and the characteristic OH band is not found in the normal spectral region. In the ' hydroxyl bond ' the hydrogen atom is still regarded as belonging to its parent oxygen, although the O–H link is somewhat weakened

and the band is observed at a lower frequency. The distance O—H··O in this type of bond is taken to be 2·7 to 2·9 Å and the energy involved about 5,000 cal./mol. Venkateswaran[16] in the course of his work on the Raman spectra of some inorganic acids came to the conclusion that, in view of the fact that the hydrogen bonds are capable of exhibiting varying bond strengths, the distinction between the two types as proposed by Bernal is too artificial.

With a view to test the validity of the generalisation namely ' the anionoid power of the donor atoms and the cationoid power of the acceptor atoms determine the strength of hydrogen bonds ' and to examine the need for division into different categories as proposed by Bernal, a large number of organic compounds containing C = O groups of different types and mixtures of these with phenol, alcohol, and chloroform have been investigated. Incidentally it was expected that the results would supplement data obtained from the study of infra-red spectra.

The experimental methods are essentially the same as those described by us in our former publications in these *Proceedings*. In this part the results of investigation of the Raman spectra of various esters and their mixtures with acceptors like phenol, methyl alcohol, ethyl alcohol and chloroform are dealt with. The following esters have been employed :

(1) Ethyl acetate, (2) Ethyl benzoate, (3) Ethyl cinnamate, (4) Phenyl acetate, (5) Phenyl propionate, (6) Phenyl benzoate, (7) Phenyl cinnamate and (8) Benzyl-acetate. In addition to the above, coumarin has been also included in this part because, as shown by us previously it behaves very much like a phenyl ester.[17]

Pure substances were available in most cases and they were further purified by repeated distillation or crystallisation. High boiling liquids were as a rule distilled under reduced pressure. Phenyl propionate was prepared by heating dry phenol with sodium propionate and propionic anhydride at 160° C. in an oil bath for six hours. It was repeatedly washed with sodium carbonate solution, ether extracted, dried over anhydrous calcium chloride and distilled under reduced pressure after the ether had been driven off. Phenyl cinnamate was prepared by the action of phenol on cinnamoyl chloride in the presence of pyridine. It was recrystallised several times from alcohol. Phenol was dried over calcium chloride and distilled perfectly out of contact with air and moisture and fresh samples were employed, because on keeping, it acquires a reddish colour which is likely to absorb much of the exciting radiation, *viz.*, 4358 Å. Methyl and ethyl alcohols were purified by distillation over calcium turnings. Chloroform was subjected to slow distillation.

A description of the spectra of the substances as recorded by us is given below and subsequently the effects of mixing the esters and the acceptor solvents on the carbonyl frequencies are dealt with. No attempt is made to give any exhaustive list of references to the previous work on the Raman Spectra of the substances because they could easily be obtained from the recent book published by Hibben.[18] However, select references relevant to the discussions are given in proper places.

Spectra of the Donor Substances in the Pure State

(Figures within brackets indicate visual estimates of the relative intensities).

(1) *Ethyl acetate.*—376 (9) 633 (9) 784 (3) 846 (10) 916 (1) 938 (1) 999 (1) 1045 (2) 1096 (1) 1114 (3) 1452 (6*b*) 1739 (6*b*) 2880 (1) 2940 (8*b*) 2982 (7*b*.)

(2) *Ethyl benzoate.*—193 (3) 214 (2) 326 (4) 395 (1) 488 (1) 588 (1) 619 (6) 677 (4) 783 (2) 809 (2) 852 (5) 1004 (10) 1029 (3) 1112 (3) 1160 (2) 1178 (2) 1277 (5) 1314 (2) 1371 (2) 1381 (2) 1453 (3) 1493 (1) 1602 (10) 1720 (8) 2935 (2) 2972 (2) 3076 (6).

(3) *Ethyl cinnamate.*—274 (1) 357 (1) 580 (1) 618 (1) 715 (2) 840 (2) 945 (2) 974 (2) 1000 (7) 1030 (3) 1153 (2) 1180 (4) 1202 (6) 1255 (2) 130 (1) 1450 (2) 1578 (2) 1598 (7) 1634 (10) 1712 (5*b*) 2940 (1) 3066 (1).

(4) *Phenyl acetate.*—185 (1) 239 (4) 272 (4) 341 (1) 529 (5) 597 (1) 618 (4) 664 (4) 694 (2) 744 (5) 815 (5) 829 (1) 892 (2) 926 (1) 1004 (10) 1027 (3) 1079 (1) 1163 (6) 1195 (6) 1262 (1) 1311 (1) 1369 (1) 1429 (1) 1448 (1) 1596 (8) 1766 (3) 2912 (2) 3047 (2) 3070 (7).

(5) *Phenyl propionate.*—186 (1) 230 (2) 268 (2) 338 (1) 529 (3) 618 (2) 660 (2) 740 (3) 820 (4) 890 (0) 926 (0) 1004 (10) 1030 (2) 1163 (3) 1195 (3) 1598 (6) 1760 (3) 2912 (1) 3072 (5).

(6) *Phenyl benzoate.*—340 (3) 610 (3) 674 (1) 850 (2) 1000 (10) 1030 (2) 1115 (2) 1158 (2) 1176 (1) 1274 (3) 1310 (1) 1365 (1) 1450 (2) 1604 (10) 1740 (7) 2930 (1) 3070 (5).

(7) *Phenyl cinnamate.*—(The spectrum was studied in solution in carbon tetrachloride.)

274 (1) 375 (1) 580 (1) 618 (1) 715 (2) 840 (2) 945 (2) 974 (2) 1000 (7) 1030 (3) 1153 (2) 1180 (4) 1202 (6) 1255 (2) 1301 (1) 1450 (2) 1540 (2) 1570 (2) 1596 (7) 1633 (10) 1742 (4) 2940 (1) 3067 (1).

(8) *Benzyl acetate.*—187 (2) 223 (2) 263 (1) 300 (1) 329 (1) 426 (0) 499 (1) 580 (5) 619 (3) 642 (2) 751 (5) 820 (1) 839 (3) 919 (2) 1002 (10) 1028 (4)

1077 (3) 1119 (3) 1157 (3) 1181 (2) 1213 (1) 1244 (1) 1263 (2) 1452 (2) 1585 (2) 1606 (8) 1745 (4) 2940 (2) 3070 (7).

(9) *Coumarin.*—(*a*) Solution in carbon tetrachloride, Frequencies between 1000–2000 cm.$^{-1}$ are given below :—

1030 (1) 1102 (3) 1125 (3) 1158 (3) 1178 (10) 1228 (4) 1257 (2) 1330 (4) 1457 (2) 1492 (2) 1570 (8) 1610 (6) 1625 (6) 1742 (6).

(*b*) Pure solid melted and resolidified.—1030 (1) 1100 (3) 1128 (3) 1156 (3) 1181 (10) 1228 (4) 1260 (4) 1328 (6) 1457 (2) 1486 (4) 1567 (8) 1604 (6) 1620 (6) 1708 (6) 1731 (6).

Spectra of Acceptor Substances

(1) *Phenol.*—236 (3) 532 (1) 624 (2) 750 (1) 812 (1) 826 (1) 1000 (10) 1028 (6) 1070 (0) 1158 (2) 1167 (3) 1255 (1) 1595 (5) 1601 (5) 3014 (0) 3046 (3) 3060 (10).

(2) *Ethyl alcohol.*—434 (1) 880 (6) 1051 (3) 1095 (3) 1453 (5) 2875 (5) 2930 (10) 2972 (4).

(3) *Methyl alcohol.*—1030 (4) 1464 (5) 2838 (5) 2945 (6).

(4) *Chloroform.*—264 (5) 367 (5) 688 (10) 765 (5*b*) 1220 (1).

In general the esters were mixed with the solvents in the proportion, 1:1 and the spectra of the mixtures compared with those of the pure substances. When solids like coumarin and phenol were concerned the two molten substances were mixed and the Raman tube containing the molten mixture was kept at about 80° C. by means of an electric heater. In many cases it was observed that the spectra of the mixtures showed conspicuous changes as far as the C = O frequency was concerned.

Mixtures of Esters with Phenol

The results obtained with these mixtures are presented in Table I. The most striking effects are noticed here; in all cases new C = O lines which are bright make their appearance and these are attributable to hydrogen bond formation as represented below :—

$$R-\underset{\displaystyle OR'}{\overset{\displaystyle O}{\overset{|}{C}}}=O \rightarrow H-O-C_6H_5.$$

Except the case of coumarin mixture, in which the original C = O frequency has completely disappeared, the others continue to exhibit the unchanged frequencies of the esters with considerably diminished intensity. Obviously the mixtures contain a portion at least of the uncombined esters. The larger

TABLE I

Name of the substance	C=O frequency in the pure state	C=O frequency in mixtures with phenols	Difference
Ethyl acetate	1739	1700, 1739	39
Ethyl benzoate	1720	1695, 1720	25
Ethyl cinnamate	1712	1685, 1712	27
Phenyl acetate	1766	1716, 1766	50
Phenyl propionate	1760	1710, 1760	50
Phenyl benzoate	1740	1704, 1740	36
Benzyl acetate	1745	1715, 1745	30
Coumarin	1742 (in CCl_4)	1710	32

shifts are noticed with esters having high C = O frequencies and *vice-versa*; the range in the values lies between 50 and 25 wave numbers.

Ester Alcohol Mixtures

Anhydrous ethyl and methyl alcohols were employed and it was noticed that the two gave identical results as far the C = O frequency shift was concerned. Here also coumarin mixtures gave a new C = O frequency, the original one having disappeared. In regard to the others the effects are not so prominent as in the case of phenol. The results are presented in Table II and the changes are attributed to the formation of hydrogen bonds of the following type :

$$R-\underset{\displaystyle OR'}{\overset{\displaystyle |}{C}}=O \rightarrow H-O-CH_3 \text{ (or } C_2H_5)$$

TABLE II

Name of the substance	C=O frequency in the pure state	C=O frequency in mixtures with alcohol
Ethyl acetate	1739	diffuse
Ethyl benzoate	1720	1722
Ethyl cinnamate	1712	1712
Phenyl acetate	1766	1746, 1766
Phenyl cinnamate	1742	diffuse
Coumarin	1742 (in CCl_4)	1720

Diffuseness of the lines mentioned above is towards shorter wavelengths and does not exceed 15 wave numbers.

Ester-Chloroform Mixtures

The tendency to form hydrogen bonds is, in general, as weak as in the case of the alcohol mixtures as will be evident from Table III.

However, coumarin, phenyl cinnamate and phenyl acetate exhibit marked shifts in the C = O frequencies even here due to complex formation as below :

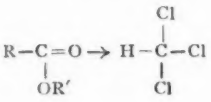


TABLE III

Name of the substance	C=O frequency in the pure state	C=O frequency in mixtures with chloroform
Ethyl acetate	1739	1736
Ethyl benzoate	1720	1722
Ethyl cinnamate	1712	diffuse
Phenyl acetate	1766	1746, 1766
Phenyl benzoate	1740	diffuse
Phenyl cinnamate	1740	1722
Benzyl acetate	1745	1740
Coumarin	1742 (in CCl_4)	1720

Diffuseness of the lines mentioned above is towards shorter wavelengths and does not exceed 15 wave numbers.

All the observed results may be consolidated and classified as follows:—

(i) Those in which a shift of the C = O frequency towards shorter wavelength is observed. The unmodified C = O frequency of the ester does not make its appearance at all in these cases. These are denoted as (*a*) in Table IV and the shifts of the C = O frequencies are given in cm.$^{-1}$ as (a_{20}) etc. Examples of this category are phenyl cinnamate in chloroform and coumarin in various solvents.

(ii) Those in which the appearance of a modified C = O frequency (towards shorter wavelengths) is noted in addition to the original C = O frequency of the ester. These are denoted by (*b*) in Table IV and the frequency differences between the two are given in cm.$^{-1}$ as (b_{20}) etc. Mixtures of most of the substances with phenol belong to this class.

(iii) This represents the cases where the C = O frequencies of the esters are found to become diffuse towards the shorter wavelengths. Cases of ethyl acetate in alcohol, phenyl benzoate in chloroform etc. belong to this group and they are represented as (*c*).

(iv) This group embodies the cases where no change has been observed in the C = O frequency of the carbonyl compound. These are denoted as (*d*).

Among the examples of this type may be mentioned the mixtures of ethyl benzoate and chloroform, ethyl benzoate and ethyl alcohol, etc.

The following table gives a consolidated statement of the changes undergone by the C = O frequencies.

TABLE IV

Name of the compound	C=O frequency of the pure substance	In chloroform	In methyl alcohol	In ethyl alcohol	In phenol
Ethyl acetate	1739	*d*	*c*	*c*	..
Ethyl benzoate	1720	*d*	*d*	*d*	b_{25}
Ethyl cinnamate	1712	*c*	*d*	*d*	b_{27}
Phenyl acetate	1766	b_{20}	b_{20}	b_{20}	b_{50}
Phenyl propionate	1760	..	..	..	b_{50}
Phenyl benzoate	1740	*c*	..	..	b_{36}
Phenyl cinnamate	1742	a_{18}	*c*	*c*	..
Benzyl acetate	1745	*d*	..	..	b_{30}
Coumarin	1742	a_{28}	a_{22}	a_{22}	a_{32}

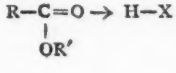
With a view to make sure that the changes observed in the C = O frequencies are not due to the effect of mere dilution, mixtures of some of the esters with the solvents benzene and carbon tetrachloride which act only as diluents were studied and Table V gives the results. The C = O frequencies are unaffected in these solvents.

TABLE V

Name of the substance	C=O frequency in pure state	C=O frequency in CCl_4 solution	C=O frequency in benzene solution
Ethyl acetate	1739	1740	1740
Ethyl benzoate	1720	1718	1721
Ethyl cinnamate	1712	1712	1712
Pheynl acetate	1766	1763	1760
Phenyl cinnamate	..	1742	1740

Discussion of the Results

From the results presented in Table IV it is clear that in a large number of cases the Raman line attributable to the C = O group has been affected. The influence of the mixture is felt in one of three ways, *viz.*, (1) a shift of the C = O line, (2) an appearance of a new line and (3) a diffuseness of the same, all taking place towards shorter wavelengths. These changes can be taken as evidences for the formation of hydrogen bonds as represented below:—



It is reasonable to assume that the extent of the lowering of the C = O frequency gives an indication of the weakening of the C = O link due to hydrogen bond formation and consequently it affords a measure of the strength of the hydrogen bond involved. From the large number of cases examined it is clear that these bonds vary very widely in strength depending upon the components of the mixtures.

Taking the series of mixtures with phenol it is evident that hydrogen bonds are formed very markedly. The strongest bonds are noticed with esters having the highest C = O frequencies. It is consequently definite that the higher the anionoid power of the C = O, *i.e.*, the greater its capacity to act as donor, the stronger is the hydrogen bond formed. Methyl and ethyl alcohols behave very similar to one another. Though as a rule the hydrogen bonds formed with these solvents are weaker than in the case of phenol, similar gradation in the strengths of the bonds with the change in the C = O frequencies are noticeable. In the case of chloroform the number of examples of hydrogen bond formation are fewer and the bonds are weaker. It is only with esters of very high C = O frequencies that any effect is noticed.

These differences in the capacities of the different solvents to form hydrogen bonds is obviously due to the differences in the cationoid power of the hydrogen atoms involved. Phenol is, of course, the best and this is to be attributed to the presence of a phenyl ring producing a positive field by withdrawing electrons as represented below :

This explains also why it behaves as a weak acid. Alcohols are comparatively weaker due to the lack of such an electron sink. However, owing to the capacity of the oxygen atom to take a negative charge the hydrogen atom attached to it is sufficiently cationoid to form hydrogen bonds. The weakness of chloroform is to be attributed to the linking of hydrogen with carbon, an atom which shows very little tendency to take a charge. In spite of the existence of three chlorine atoms which produce positive inductive effect, the cationoid power of the hydrogen is small compared with some of the hydroxylic compounds. This agrees with the general behaviour of carbon compounds wherein even the reactive methylene groups exhibit very little tendency to produce hydrogen ions. Thus the general expectation that the strengths of hydrogen bonds depend upon (1) the anionoid power of the donor and (2) the cationoid power of the acceptor is amply substantiated.

Further cases of hydrogen bond formation leading to a full discussion of the results will be described in the subsequent communications.

Summary

A brief survey of the existing literature on hydrogen bonds is made. The advantages of employing the Raman effect for investigations in this field are discussed. The results not only supplement those obtained from infra-red studies but they become more definite, particularly when such groups as the C = O, which yield sharp Raman lines, are employed.

Hydrogen bond formation between various esters as donor molecules and phenol, alcohols and chloroform as acceptor molecules has been studied and the results are presented in this paper. The changes in the C = O frequencies are classified. It is shown that there are large variations in the strengths of hydrogen bonds. The generalization that the strengths of hydrogen bonds depend on the anionoid power of the donor and the cationoid power of the acceptor atoms is made as a logical consequence of the mechanism of hydrogen bonds and is supported by the experimental results that are recorded.

REFERENCES

1. Moore and Winmill .. *J. Chem. Soc.*, 1912, **101**, 1635.
2. Huggins .. *Undergraduate Thesis*, University of California, 1919.
3. Latimer and Rodebush .. *J. Amer. Chem. Soc.*, 1920, **42**, 1419.
   Lewis .. *Valence and Structure of Atoms and Molecules*, Chemical Catalogue Co., N.Y., 1923, 110.
4. Sidgwick .. *J. Chem. Soc.*, 1925, **127**, 907.
5. ———— .. *Ann. Reports Chem. Soc.*, 1933, 112.
6. .. *Trans. Farad. Soc.*, 1940, **36**, 871.
7. Pauling and Brockway .. *Proc. Nat. Acad. Sci.*, 1934, **20**, 336.
8. Hendricks, Hilbert, Wulf and Liddel *Nature*, 1935, **135**, 147.
9. Freymann .. *J. Chem. Phys.*, 1938, **6**, 497.
10. Buswell, Dietz and Rodebush .. *Ibid.*, 1937, **5**, 84, 501.
11. Errera and Mollet .. *Nature*, 1936, **138**, 882;
    Fox and Martin .. *Proc. Roy. Soc.*, 1937, **162 A**, 419.
12. Williams and Gordy .. *J. Amer. Chem. Soc.*, 1937, **59**, 817 (This contains references to the previous work).
13. Cross, Burnham and Leighton .. *Ibid.*, 1937, **59**, 1134;
    Venkateswaran .. *Vide* Reference No. 16;
    Koteswaram .. *Z. physik*, 1938, **110**, 118; 1939, **112**, 404;
    Murty and Seshadri .. *Proc. Ind. Acad. Sci.*, 1938, **8**, 519; *Curr. Sci.*, 1939, **8**, 209;
    Saksena .. *Proc. Ind. Acad. Sci.*, 1940, **11**, 53;
    Sunandabai .. *Ibid.*, 1940, **11**, 212.
14. Rodebush and Buswell .. *J. Phys. Chem.*, 1939, **43**, 219.
15. Bernal and Megaw .. *Proc. Roy. Soc.*, 1935, **151**, 384.
    Bernal .. *Trans. Farad. Soc.*, 1937, **33**, 210.
16. Venkateswaran .. *Proc. Ind. Acad. Sci.*, 1938, **7**, 13.
17. Murty and Seshadri .. *Ibid.*, 1939, **10**, 307.
18. Hibben .. *The Raman Effect and its Chemical Applications* (Reinhold Publishing Corporation).

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ERRATA

Volume XIV, No. 4, Section A, 1941

Page 365, line 38 *for* 41,000 k.v. *read as* 41,000 v.

Page 372, line 27 *for* $\frac{e^{-h\nu^0/kT}+1}{e^{-h\nu^0/kT}-1}$ *read as* $\frac{e^{h\nu^0/kT}+1}{e^{h\nu^0/kT}-1}$

Page 389, Figure 1 *for* Scale $\frac{1}{3}$ full size *read as* scale 1/6 full size.

Plate XXIV, Figure 8 *for* 4346 *read as* 4046° A.

Pages 415–20, *for* Hexamethyl-tetramine *read as* hexamethlene-tetramine.

Page 431, Table III, line 6 *for* (400) reflections *read as* 2 (200) reflections.

Page 431, Table III, line 6 *for* (600) reflections *read as* 3 (200) reflections.

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ERRATA

Vol. XIV, No. 3, Section A, 1941

Page 313, para 2, line 5 *for* quadric "Σ'_1" *read* quadric "Σ',".

„ 313, „ 4, „ 3 *for* "$2\,U_i lt$" *read* "$2\,U_i lp$".

„ 313, „ 4, „ 4 *for* "V_i" *read* "U_i".

„ 315, „ 1, „ 3 *for* "ψ_2" *read* "ψ_α".

„ 315, „ 1, „ 2 in the equation, *for* "$-\psi_\alpha\,(a\,S_{1\delta}+S_{1\alpha})$" *read* "$-\psi_\alpha\,(a\,S_{1\delta}+d\,S_{1\alpha})$".

„ 315, „ 2, „ 2

for "$2\,S_{iA}=\dfrac{\partial\,S_i\,(V)}{\partial\,A}, \cdots, \cdots, \cdots, \psi_A=a\,A+b\,B+$"

read "$2\,S_{1A}\equiv\dfrac{\partial\,S_i\,(V)}{\partial\,A}, \cdots, \cdots, \cdots, \psi_A\equiv a\,A+b\,B+$".

„ 315, line 2 from bottom *for* "$P'\mu$ w.r.t." *read* "$\mu\,P'$ w.r.t."

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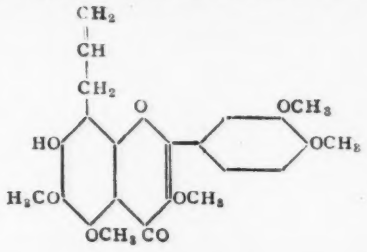
ERRATA

Page 291, Vol. XIV, No. 3, September 1941

Constitutional formula (V) should be as follows: